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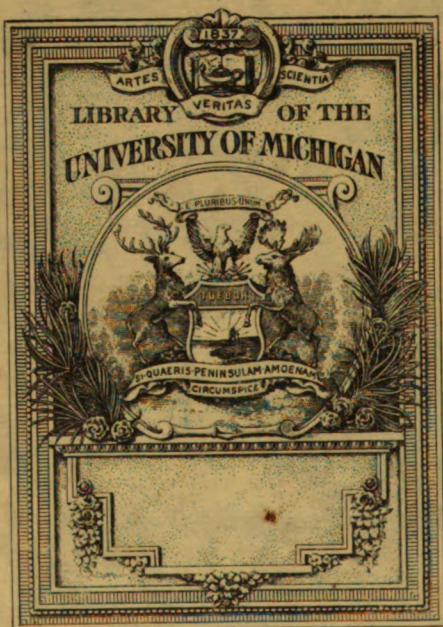
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INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus:—*Annalen*, 221, 92, instead of *ccxxi*, 92.

5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

6. As a rule, details of methods of preparation or analysis, or generally speaking of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

Nomenclature.

7. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radicles with the group OH, *hydroxides* and not *hydrates*; for example, potassium hydroxide, phenyl hydroxide, the name *hydrate* being reserved for compounds supposed to contain water of combination or crystallization. Compounds such as CH_3ONa , $\text{C}_2\text{H}_5\text{ONa}$, $\text{C}_7\text{H}_7\text{ONa}$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3 , H_2SO_4 , H_3PO_4 , and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulae*.

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the $\text{C}_n\text{H}_{2n+2}$ series of the form $\text{CH}_3\cdot[\text{CH}_2]_n\cdot\text{CH}_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane; for example, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3 = \text{propylmethane}$; $\text{CH}_3\cdot\text{CH}(\text{CH}_3)_2 = \text{isopropylmethane}$ or *trimethylmethane*; or, although less frequently, by names such as *diisopropyl*.

11. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not *ethene* and *ethine*). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as *methylethylene*, *dimethylethylene*, &c., denoting the di-derivatives of the form $\text{C}_n\text{H}_{2n+1}\cdot\text{CH}:\text{CH}\cdot\text{C}_n\text{H}_{2n+1}$, as α -, and those of the form $\text{CH}_2\cdot\text{C}(\text{C}_n\text{H}_{2n+1})_2$ as β -compounds, thus: $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}_3 = \alpha\text{-dimethylethylene}$; $\text{CH}_3\cdot\text{C}(\text{CH}_3)_2 = \beta\text{-dimethylethylene}$. Similarly, use names such as *methylacetylene* and *dimethylacetylene* for the homologues of acetylene of the form $\text{CH}:\text{C}\cdot\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n+1}\cdot\text{C}:\text{C}\cdot\text{C}_n\text{H}_{2n+1}$. Adopt the same *allens* for the hydrocarbon $\text{CH}_2\cdot\text{C}:\text{CH}_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*; such as *quinol*, *catechol*, *resorcinol*, *saligenol*, *glycerol*, *erythrol*, *mannitol*, instead of *hydroquinone*, *pyrocatechin*, *resorcin*, *saligenin*, *glycerin*, *erythrite*, *mannite*. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write *indole* instead of *indol*; *furfuraldehyde* instead of *furfurol*; *fucusaldehyde* instead of *fucusol*. Ethers derived from phenols, such as $\text{C}_6\text{H}_5\cdot\text{OCH}_3$, &c., hitherto called *anisol*, *anethol*, &c., may be distinguished by names ending in *oil*, as *anisoil* and *anethoil*.

Alcohols should be spoken of as *mono*-, *di*-, *tri*-, or *n-hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not *oxy*-derivatives; for example, *hydroxyacetic* and not *oxyacetic* acid. Compounds containing the analogous groups $\text{C}_2\text{H}_5\text{O}$, $\text{C}_6\text{H}_5\text{O}$, $\text{CH}_3\cdot\text{COO}$, &c., should in like manner be termed *ethoxy*-, *phenoxy*-, *acetoxy*-derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2COOH$, and not $C_6H_3(OC_2H_5)_2COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

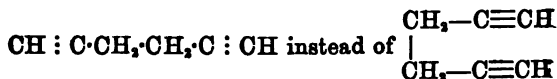
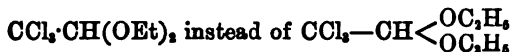
15. Compounds of the radicle SO_2H should, whenever possible, be termed *sulphonic acids*, or failing this, *sulpho-compounds*: as benzene-sulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle SO_2NH_2 should be termed *sulphonamides*.

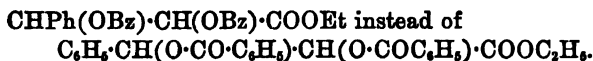
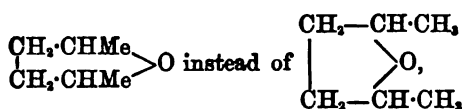
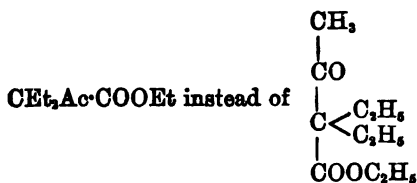
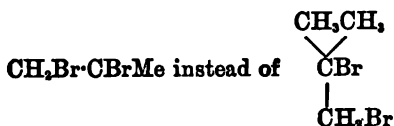
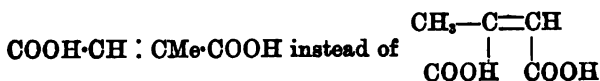
16. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

Notation.

17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

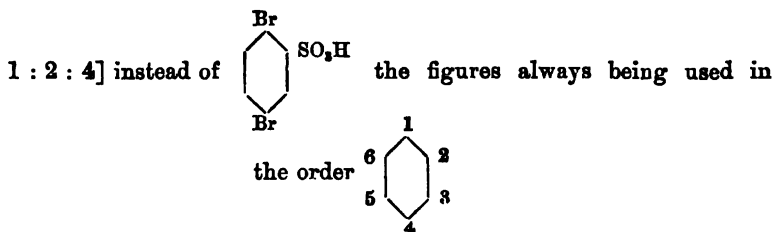
18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3 , Et for C_2H_5 , Pr^a for $CH_3CH_2CH_3$, Pr^s for $CH(CH_3)_3$, Ph for C_6H_5 , Ac for $COCH_3$, and Bz for COC_6H_5 ; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:





19. In representing the constitution of benzene-derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example:—

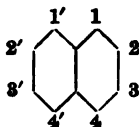
Paradibromobenzenesulphonic acid, $\text{C}_6\text{H}_4\text{Br}_2\text{SO}_3\text{H}$ [Br : SO_3H : Br =



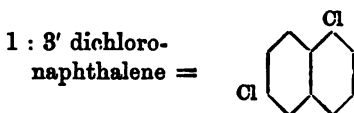
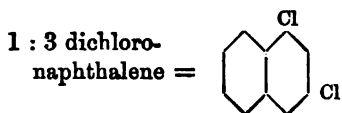
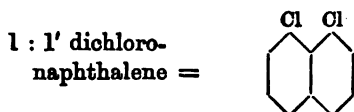
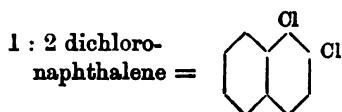
Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them *ortho*- or *meta*-dibromobenzene, &c.

20. Moreover, in representing the constitution of derivatives of other "closed-chain" hydrocarbons do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner:—

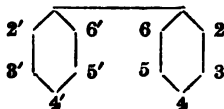
In the case of *naphthalene*, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1', 2', 3', 4' in the order shown by the annexed symbol:—



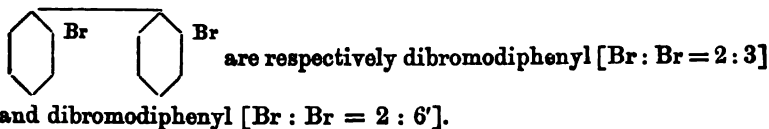
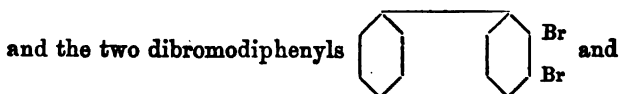
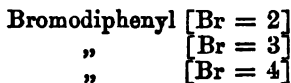
The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene[Cl : Cl = 1 : 2], &c., thus:—



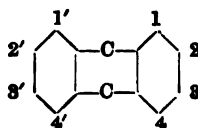
In the case of *diphenyl*, indicate the position of the radicles relatively to the carbon-atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures, 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2', 3', 4', 5', 6'. as shown by the following symbol:



Thus the mono-derivatives, the bromodiphenyls, for example, are represented as



In the case of *anthracene*, employ the following symbol, and indicate the position of the radicles relatively to the central C_2 -group:



Examples:

Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$, [OH : OH = 1 : 2].

Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$, [OH : OH = 1 : 4].

Anthraflavic acid, $C_6H_3(OH) : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 2 : 3].

Purpurin, $C_6H_4 : C_2O_2 : C_6H(OH)_3$, [OH : OH : OH = 1 : 2 : 4].

In speaking of compounds such as these, their constitution may be represented by the names

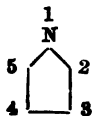
1 : 2 Dihydroxyanthraquinone	= Alizarin.
1 : 4	" = Quinizarin.
2 : 3'	" = Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquinone	= Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

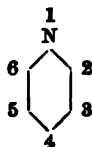
21. In the case of *thiophen*, express the position of the radicles introduced relatively to the sulphur-atom by numbers, as shown by the following symbol:



In the cases of *pyrroline* and *pyridine*, indicate the position relatively to the nitrogen-atoms as shown by the following symbols:

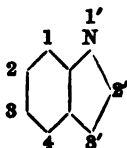


Pyrroline.

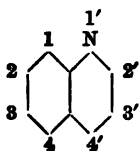


Pyridine.

In the case of *indole*, positions should be numbered as shown in the following symbol:—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1', 2', 3', 4' in the order shown by the annexed symbol:—



The Editor's decision, in all matters connected with the Abstracts, must be considered final.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

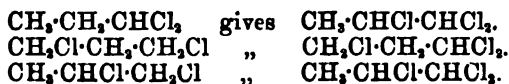
Organic Chemistry.

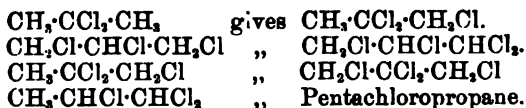
Substitution of Chlorine and Bromine in the Fatty Series.
By A. D. HERZFELDER (*Ber.*, 26, 2432—2438).—The following is a translation of the author's own summary of his results.

When into a monohalogen compound a second halogen atom is introduced, it always attaches itself to that carbon atom which is situated next to the carbon atom already united with halogen. In the case of further substitution, this rule only holds for bromine, of which it is never possible, by other than violent means, to attach more than 1 atom to each atom of carbon. On the other hand, when a third atom of chlorine is introduced, it frequently attaches itself to a carbon atom that is already united with chlorine.

Bromides that already contain 1 atom of bromine united with each atom of carbon, cannot easily be further brominated; chlorides, however, take up more chlorine. A normal hydrocarbon, when brominated by ordinary means, takes up as many atoms of bromine as it contains atoms of carbon; this was shown in the case of methane, ethane, propane, and also, although not with absolute certainty, in that of butane, hexane, heptane, and octane.

The chloropropanes yielded the following compounds on further chlorination.





C. F. B.

Formation of Ethereal Salts by Double Decomposition. By G. BERTONI (*Chem. Centr.*, 1893, ii, 362—363; from *Arch. sci. phys. nat. Genève*, 15, 1—23).—Ethereal salts may be obtained by double decomposition in a similar way to inorganic salts; and when one of the products of the reaction is removed from the sphere of action as it is formed, the action is complete.

If methylic alcohol is gradually added to pure glyceric nitrite at the ordinary temperature, a brisk reaction sets in, and 97 per cent. of the theoretical yield of methylic nitrite distils over. The reaction is somewhat less complete with ethylic alcohol, and still less so with isopropylic, isobutylic, and amylic alcohols.

The same double decomposition may be brought about in a sealed tube, provided that the final products will separate into two layers. When the nitrite of ethylene glycol is prepared in this way by mixing glyceric nitrite and glycol, a homogeneous opalescent liquid is obtained which separates into two layers when heated or when mixed with dry ether.

A comparison of the boiling points of the alcohols and their nitrites shows a very simple relation.

	Amylic.	Iso-butylic.	Iso-propylic.	Ethylic.	Methylic.
B. p. of alcohol..	132°	107°	84°	78°	67°
B. p. of nitrite..	92	67	44	18	—13

The difference in the boiling points is 40°, or 40° + $\frac{1}{2}$ ° for ethylic alcohol and 2 × 40° for methylic alcohol.

The author has prepared the following ethereal salts by this method. *Allylic nitrite* is a limpid, yellowish liquid which has the sp. gr. 0.9546, and boils at 43.5—44.5°. The boiling point of allylic alcohol is 96°, and the boiling point of the nitrite is 96° — (40° + $\frac{1}{2}$ °) = 46°. *Ethylenic nitrite* is a limpid, yellowish liquid which has a very unpleasant odour, is poisonous, and boils at 96—98°; the sp. gr. = 1.2156. The boiling point calculated from the boiling point of the glycol (197°) by the formula 197° — (2° × 40° + $\frac{2}{3}$ °) = 97°. The *tertiary butylic nitrite* is a limpid, pale yellow liquid which has an unpleasant odour, and boils at 62.8—63.2°; the sp. gr. = 0.8914. The boiling point is calculated from the equation 83° — $\frac{1}{2}$ ° = 63°.

E. C. R.

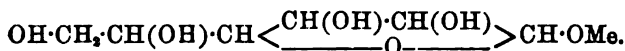
Preparation and Properties of Potassium Cyanate. By H. ERDMANN (*Ber.*, 26, 2438—2443).—Potassium cyanate may be conveniently prepared in the following manner; it is not advantageous to use larger quantities in one operation than those given. 200 grams of completely dehydrated potassium ferrocyanide, while still warm, is triturated with 150 grams of fused potassium dichromate, and the mixture heated in a large nickel or iron dish. The black product is

powdered, and boiled on the water bath, with frequent shaking, for 10 minutes with a mixture of 900 c.c. of 80 per cent. alcohol and 100 c.c. of methylic alcohol. The clear solution is then decanted through a folded filter into a large beaker standing in ice and water; the vessel containing the black residue is also placed in ice and water to prevent decomposition. Potassium cyanate separates out in the beaker, and is drained on a filter with the pump; the mother liquor is used again to extract the black residue, as above, the process being repeated three or four times. The accumulated cyanate (about 65 grams) is then washed with ether and dried in a vacuum over sulphuric acid; it is nearly pure, containing only a trace of carbonate. The alcoholic mother liquor cannot be worked up for cyanate by boiling it down, for the cyanate then completely decomposes into carbonate and ammonia; carbamide may, however, be obtained from it by adding ammonium sulphate (70 grams), evaporating to dryness, and extracting the residue with 96 per cent. alcohol. C. F. B.

Antimony-blue. By G. SEBOR (*Chem. Centr.*, 1893, ii, 318—319; from *Casopis proprusmysl chemicky*, 3, 216).—Antimony-blue is prepared by dissolving antimony sulphide in concentrated hydrochloric acid, and, after filtering, adding to the boiling liquid a concentrated solution of potassium ferrocyanide and some potassium chlorate or nitric acid; the precipitate is dried at 100°. An antimony-blue is also obtained by mixing antimony chloride and potassium ferrocyanide, and adding a large quantity of water. When prepared in this way, it contains some basic antimony chloride. A sample of pure antimony-blue gave, on analysis, Fe = 30.28, Sb = 2.422, H₂O = 5.828, Cl = 0.712, O = 0.323, and CN = 60.435 per cent. The blue is insoluble in cold hydrochloric, sulphuric, and nitric acids; when boiled with hydrochloric or sulphuric acid, it yields hydrocyanic acid. Dilute sodium and potassium hydroxides and ammonia only attack it when warmed. When heated with nitric acid, it is converted into a greyish-green compound. Unlike Prussian-blue, it is not soluble in a solution of an oxalate or tartrate. E. C. R.

Glucosides of the Alcohols. By E. FISCHER (*Ber.*, 26, 2400—2412).—A number of sugars have been found to form condensation products of the nature of glucosides, with alcohols and hydroxy-acids. These compounds do not react with alkalis, with Fehling's solution, or with phenylhydrazine, but they are decomposed, although more slowly than cane sugar, by boiling with dilute acids, or by the action of invertase or active yeast, into the original alcohol and sugar. That they do not react with phenylhydrazine shows that they no longer contain a carbonyl group; this group in the original sugar must therefore have taken part in the condensation. As for the hydroxyl, which must also have contributed to the water formed in the reaction, it cannot have been that united with the α carbon atom, for the product obtained (this vol., i. 38) by condensing an alcohol with benzoïn (which contains a CH \cdot OH group in the α -position to a CO group), does react with phenylhydrazine. It is most probable that the γ -hydroxyl group is the one concerned, and, in this case, the

product formed from methylic alcohol and glucose with loss of water will have the formula



These compounds are named by combining the name of the alcohol with that of the sugar; thus, ethylrhamnoside denotes the condensation product formed from ethylic alcohol and rhamnose. They are prepared by dissolving the sugar in the alcohol, and saturating the solution in the cold with gaseous hydrogen chloride; when the sugar is insoluble in the alcohol, it is dissolved in a little water, and the solution mixed with excess of a saturated alcoholic solution of hydrogen chloride, or an acetyl derivative of the sugar may be dissolved in the alcohol, and the solution saturated with hydrogen chloride, in which case the same product is obtained as when the sugar itself is used. For details of the process by which the product is purified and obtained crystallised, reference must be made to the original paper. Most of these substances are sweet, but benzylglucoside and ethylrhamnoside are bitter.

Methylglucoside, $\text{C}_6\text{H}_{11}\text{MeO}_5$, forms colourless crystals, melts at $165\text{--}166^\circ$ (uncorr.), and has specific rotation $[\alpha]_{\text{D}}^{20} = +157.5^\circ$. *Methylarabinoside*, $\text{C}_6\text{H}_9\text{MeO}_5$, crystallises in colourless needles or plates, and melts at $169\text{--}171^\circ$ (uncorr.). *Ethylarabinoside*, $\text{C}_8\text{H}_{11}\text{EtO}_5$, forms stellate groups of crystals, and melts at $132\text{--}135^\circ$ (uncorr.). *Ethylrhamnoside* is a colourless, bitter syrup; so is *methylrhamnoside*. *Ethylglucoside* was obtained as a partly crystalline, partly amorphous, mass, and is identical with the "diglucose" of Gantier (*Bull. Soc. Chim.*, [2], 22, 145). *Benzylglucoside* was also obtained as a bitter, partly crystalline, partly amorphous, mass. *Glycolglucoside* forms a colourless syrup. *Lactic acid glucoside* was obtained as a hygroscopic, white powder.

C. F. B.

Quinovose and "Quinovite." By E. FISCHER and C. LIEBERMANN (*Ber.*, 26, 2415—2420).—"Quinovite" is shown to be really *ethylquinovose*, $\text{C}_8\text{H}_{11}\text{EtO}_5$, for it is converted by boiling with dilute acids into ethylic alcohol and a sugar, to which the name *quinovose* is given. Quinovose is shown, by analysis of its osazone, to have the composition $\text{C}_8\text{H}_{11}\text{O}_5$; further, it yields 2:5-methylfurfuraldehyde when distilled with dilute hydrochloric acid, and so must be a methylpentose, $\text{OH}\cdot\text{CHMe}\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{CHO}$. From this follows the formula given above for "quinovite," which agrees well with the analyses of the substance, and of its triacetyl derivative published by Liebermann and Giesel (*Ber.*, 16, 935; *Abstr.*, 1884, 1191).

Quinovose was obtained as a yellowish syrup with a sweet, at the same time slightly bitter, taste; it is oxidised by bromine water to an acid, readily reduces Fehling's solution, and with phenylhydrazine yields *phenylquinovosazone*, $\text{C}_8\text{H}_{10}\text{O}_5(\text{N}_2\text{HPh})_2$, which crystallises in minute, yellow needles, and melts at $193\text{--}194^\circ$ (uncorr.).

C. F. B.

Action of Lime and Alkalis on Invert Sugar. By L. JESSER (*Chem. Centr.*, 1893, ii, 364—365; from *New. Zeit. Rüb.-Zucker-Ind.*

31, 3—11).—A 0·2—0·4 per cent. solution of glucose was treated with different quantities of lime, and the product, after precipitating the lime with carbonic acid, was examined, and the lime and dry substance determined in it. With moderate proportions of lime, and at temperatures below the boiling point, 100 grams of glucose gave 109·8 grams of dry substance containing 16·85 parts of calcium (? oxide) and 92·95 parts of organic matter. With a more intense action of the lime, 102·4 grams of dry substance was obtained, containing 16·7 parts of calcium (? oxide) and 85·7 parts of organic constituents. This product is not altered by prolonged boiling with caustic lime. A solution of lævulose, treated in the same way, is at 80° already converted into products which are unaltered by boiling with lime, that is, the lime acts more readily on lævulose than on glucose. From the above results, it is possible to calculate the quantity and composition of the product formed by the action of lime on invert sugar; and the author obtained by experiment numbers which agreed with those calculated. The products are neutral calcium salts which are not optically active, do not reduce Fehling's solution, and, when treated with sulphuric acid, yield volatile acids.

When a mixture of alkali and lime is employed in the place of lime alone, similar products are obtained containing the alkali in place of lime.

The ratio of the lime combined with these acids to that of the glucose employed is $1\frac{1}{2}$ mol. of calcium (? oxide) to 2 mols. of glucose, and this ratio is not altered by boiling with excess of alkali.

E. C. R.

Resolution of Starch by the Action of Diastase. By C. J. LINTNER and G. DÜLL (*Ber.*, 26, 2533—2547).—By the action of phenylhydrazine on beer extract, isomaltosazone is formed, but at present it is uncertain whether the compound is identical with that of E. Fischer, and of Scheibler and Mittelmeier. The authors criticise the theory of Brown and Morris on the resolution of the starch molecule (*Trans.*, 1889, 449) and suggest that the various amyloins are merely mixtures of dextrin and isomaltose. Five definite compounds are formed by the action of diastase on starch, namely, isomaltose and maltose, and three dextrans, for which the names amylodextrin, erythro-dextrin, and achroodextrin are suggested. These substances were isolated by treating the solutions with alcohol of various strengths; their purity was determined by means of the refractive power, molecular weight by Raoult's method, and their behaviour towards phenylhydrazine, alkaline copper solution, and iodine in the manner fully described in the original paper.

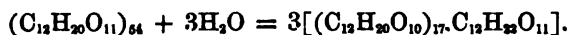
Amylodextrin, $(C_{12}H_{20}O_{10})_{54}$, the first decomposition product of starch, is a fine, white powder; it is sparingly soluble in cold water, but dissolves on heating in almost every proportion, and readily forms supersaturated solutions; spheroidal crystals are readily deposited from solutions containing 20—30 per cent. The refractive power $[\alpha]_D = 196^\circ$. The compound gives a deep blue coloration with iodine, and does not reduce alkaline copper solution. Amylodextrin is the chief constituent of "amidulin," "soluble starch," &c.

Erythro-dextrin, $(C_{12}H_{20}O_{10})_{18} + H_2O = (C_{12}H_{20}O_{10})_{17} \cdot C_{12}H_{22}O_{11}$, is

formed by the action of diastase on the preceding compound, and is deposited from dilute alcoholic solution in spheroidal crystals. It reduces alkaline copper solution, and gives a reddish-brown coloration with iodine. The refractive power $[\alpha]_D = 196^\circ$.

Achroodextrin, $(C_{12}H_{20}O_{10})_6 + H_2O = (C_{12}H_{20}O_{10})_5 \cdot C_{12}H_{22}O_{11}$, is extremely soluble in water; in alcoholic solution crystals are formed which could not be isolated. It readily reduces alkaline copper solution, gives no coloration with iodine, and has a slight sweet taste. The refractive power $[\alpha]_D = 192^\circ$.

Isomaltose, $C_{12}H_{22}O_{11}$, has not yet been obtained in crystals; it undergoes fermentation in presence of yeast, is converted into maltose by the action of diastase, and readily reduces copper solution. The refractive power $[\alpha]_D = 140^\circ$. The osazone (see above) melts at $150-153^\circ$. The successive stages in the decomposition of amylo-dextrin by the action of diastase are represented by the following equations.



Erythrodextrin.



Achroodextrin.



Isomaltose.

Maltose.

The authors point out that in ordinary circumstances all these changes occur simultaneously. J. B. T.

Soluble Gums. By P. PALLADINO (*Bull. Soc. Chim.*, [3], 9, 578—580).—Soluble gums never contain starch. The presence of dextrin is difficult to recognise, but if an alkaline solution of a gum is boiled for a minute with aniline sulphate, chlorobrucine, pure brucine, orcinol, or orcein, the liquid remains pale yellow with a greenish tinge, in the absence of dextrin, but becomes orange-yellow or brownish-red if the latter is present. Other results are given in the following table. (1) is the sp. gr. at 15° of solutions con-

	1.	2.	3.	4.
Kordofan.....	1.0450	1.4166	6.29	—26.47
Galam.....	1.0448	1.3333	7.23	+ 2.11
Salabreda.....	1.0448	1.4166	8.18	+14.57
Bas du Fleuve.....	1.0450	1.5000	6.92	—28.47
Arabic (Kordofan)....	1.0454	1.3333	6.92	—23.02
Zula.....	1.0448	1.1666	7.23	+12.84
Gheziri.....	1.0446	1.3333	9.75	+45.01
Amrad.....	1.0425	1.3333	5.03	+71.81
Australia.....	1.0438	1.1666	5.03	+62.21
Cape.....	1.0395	1.5000	7.86	+33.09
Snakim.....	1.0450	1.3333	10.06	—21.17
Turique.....	1.0450	1.5833	9.12	+34.41
Geddah.....	1.0449	1.4166	5.34	—24.87

taining 13.024 grams of the gum in 100 c.c.; (2) is the viscosity of the same solution as compared with water; (3) is the acidity in terms of arabic acid; (4) is the specific rotation, $[\alpha]_D$, at 16°.

The rotatory powers of solutions of different parts of the same fragment of gum are different. There is no constant relation between the rotatory power of the gum solution and the quantity of gummie acid obtainable from it; neither is there any relation between the rotatory power of the gum and that of the sugars obtained from it by the action of acids.

C. H. B.

Dimethylbutylamine. By P. ESCHERT and M. FREUND (*Ber.*, 26, 2490—2493; compare Abstr., 1891, 1172).—Dimethylbutylamine, $\text{CMe}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}_2$, is prepared by the reduction of ethyldimethylacetone-nitrile; it boils at 113—114°, and readily absorbs water and carbonic anhydride; the *hydrochloride*, $\text{C}_6\text{H}_{15}\text{N}\cdot\text{HCl}$, crystallises from a mixture of alcohol and ether, and melts at 225—228°. The *platinochloride*, $(\text{C}_6\text{H}_{15}\text{N})_2\text{H}_2\text{PtCl}_6$, crystallises from water, and decomposes at about 210°. The *aurochloride*, $\text{C}_6\text{H}_{15}\text{N}\cdot\text{HAuCl}_4$, crystallises in needles. The *phenylthiocarbamide*, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CMe}_2\text{Et}$, is deposited from alcohol in needles melting at 120—121°. The *phenylcarbamide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CMe}_2\text{Et}$, melts at 103—105°. *Dihexyloxamide*, $\text{C}_6\text{O}_2(\text{NH}\cdot\text{CH}_2\cdot\text{CMe}_2\text{Et})_2$, crystallises from alcohol in needles, and melts at 102°. By the action of silver nitrite on the hydrochloride, an alcohol is obtained which boils at 119—122°; it has the formula $\text{C}_6\text{H}_{15}\text{O}$, but the quantity obtained was too small to determine whether it was methyl-diethylcarbinol (b. p. 121—122.5°), or dimethylpropylcarbinol (b. p. 122.5—123.5°); the authors suggest that it is the former compound. Allylamine hydrochloride, when treated with silver nitrite, yields allylic alcohol, but no acetone.

J. B. T.

Guanidine Derivatives of Bibasic Acids. By W. TRAUBE (*Ber.*, 26, 2551—2558).—Guanidine reacts with ethylic oxalate and ethylic malonate to form derivatives which correspond in composition and chemical properties with parabanic acid and barbituric acid, the urea residue of these being replaced by the guanidine residue.

Oxalylguanidine, $\text{HN}\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, is precipitated by acetic acid from its solution in ammonia, in the form of white crystals containing $1\text{H}_2\text{O}$, which is lost at 160°. The anhydrous compound is insoluble in alcohol and ether, slightly soluble in water. It readily dissolves in alkalis, but decomposes into oxalic acid and guanidine when the solutions are allowed to remain in the cold, or more rapidly on boiling. It dissolves in concentrated mineral acids, and may be recrystallised from hot dilute hydrochloric acid. When heated, it decomposes without melting.

Malonylguanidine, $\text{CH}_3\cdot\text{C}\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ | \\ \text{CO}\cdot\text{NH} \end{smallmatrix}\cdot\text{C}\cdot\text{NH}$, also crystallises with $1\text{H}_2\text{O}$, which is lost at 110°. It is slightly soluble in hot water, almost insoluble in cold water and alcohol, and dissolves in alkali, alkali carbonates, ammonia, and concentrated acids. When boiled.

with alkalis, it is decomposed into guanidine and malonic acid. It behaves as a monobasic acid, and forms a *barium salt*, $(C_4H_5N_3O_2)_2Ba + 8H_2O$, which is only slightly soluble in cold water. The *calcium salt* is readily soluble in hot, slightly in cold, water. *Dibromomalonylguanidine*, $C_4H_3Br_2N_3O_2$, is prepared by the direct action of bromine on malonylguanidine. It forms slender, almost colourless needles, and when heated decomposes with evolution of bromine vapour without previously melting. It is insoluble in alcohol and ether, slightly soluble in hot water, and dissolves readily in alkalis. It is not altered by boiling with water, but is decomposed by boiling aqueous alkalis. *Nitromalonylguanidine*, $HN:C(NH:CO)_2:CH:NO_2$, obtained by the action of fuming nitric acid on malonylguanidine, is a faintly yellowish, crystalline powder, which deflagrates when gently heated. Like dilituric acid, the corresponding urea derivative, it dissolves in alkalis with an intense yellow colour. The *ammonium*, *sodium*, and *calcium salts* are yellow, crystalline substances, only slightly soluble in cold water.

Isonitrosomalonylguanidine, $HN:C(NH:CO)_2:C:NOH$, is formed by the action of nitrous acid on malonylguanidine. The *ammonium salt*, which forms lustrous, violet blue crystals containing $1H_2O$, decomposes on heating, some ammonia being evolved along with the water. It is very slightly soluble in cold, more readily in hot, water. Aqueous potash converts it into the *potassium salt*, which forms dark rose-red plates. The *sodium salt* is dark violet, and forms a purple solution in water. The *calcium salt*, with $4H_2O$, forms very slender, light red needles. The free isonitrosomalonylguanidine is separated from its salts, on treatment with dilute sulphuric acid, as a greyish green, slimy mass, which is insoluble in water, and becomes red when boiled with water or exposed to the air. It dissolves in concentrated acids, and is oxidised by nitric acid to the nitro-compound.

Amidomalonylguanidine, $HN:C(NH:CO)_2:CH:NH_2$, is obtained by the action of hydrogen sulphide on a solution of isonitrosomalonylguanidine in hydrochloric acid. When the ammonium salt of the isonitroso-compound is boiled with a solution of ammonium hydrogen sulphite, a colourless solution is formed, from which crystals separate on cooling; these have the composition



and correspond with the ammonium salt of thionuric acid in the urea derivatives. On treatment with dilute acids, this substance decomposes with formation of sulphuric acid and amidomalonylguanidine, the sulphate of which crystallises out on cooling. Amidomalonylguanidine is a yellowish powder which is scarcely soluble in water, and rapidly becomes dark red when exposed in a moist state to the air. It dissolves in acids, with which it forms crystalline salts, and is also soluble in alkalis. Both the base and its salts reduce ammoniacal silver solution, and are oxidised by the halogens or concentrated nitric acid with formation of oxalylguanidine. When an ammoniacal solution of the amido-base is oxidised by a current of air, or by

mercuric oxide, a solution is obtained resembling in colour a concentrated permanganate solution. The compound formed, which possibly corresponds with murexide, is very unstable, and could not be isolated.

Imidopseudouric acid, $\text{HN} \cdot \text{C}(\text{NH} \cdot \text{CO})_2 \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, is prepared by dissolving the amido-compound in a boiling concentrated solution of potassium cyanate. It crystallises with $1\text{H}_2\text{O}$, which is lost at 135° , and is readily soluble in hot water, from which it separates on cooling in lustrous, slightly yellowish needles. The yellow *silver salt* rapidly decomposes with separation of silver.

A. H.

Properties and Constitution of Hydroxylamine and its Homologues. By J. W. BRÜHL (*Ber.*, **26**, 2508—2520).—Hydroxylamine was prepared by Lobry de Bruyn's method by the action of sodium methoxide on hydroxylamine hydrochloride, and the product fractionated in a vacuum. The yield is 66 per cent. of the theoretical. The preparation of methylhydroxylamine and of ethylhydroxylamine has been recently described by Kjellin (next abstract); the instability of the latter compound probably accounts for the variations in its physical constants. The following results have been obtained. Hydroxylamine, sp. gr. $0^\circ/4^\circ = 1.2255$; $23.5^\circ/4^\circ = 1.2044$. $M_a = 7.193$; $M_{Na} = 7.228$; $M_\gamma - M_a = 0.190$. The refractive indices were determined at 23.5° . Methylhydroxylamine, sp. gr. $20^\circ/4^\circ = 1.0003$; $M_a = 11.74$; $M_{Na} = 11.80$; $M_\gamma - M_a = 0.31$. Ethylhydroxylamine, sp. gr. $63.9^\circ/4^\circ = 0.9079$; $M_a = 16.78$; $M_{Na} = 16.83$; $M_\gamma - M_a = 0.39$.

In the course of some hitherto unpublished work, the author has determined the refractive powers of ethylamine and of methylamine. The results are: Methylamine, $M_a = 10.23$; $M_{Na} = 10.25$; $M_\gamma - M_a = 0.29$. Ethylamine, $M_a = 14.80$; $M_{Na} = 14.85$; $M_\gamma - M_a = 0.40$. With the help of these values, and knowing the refractive power of ammonia, and of CH_3 , it is possible to calculate the separate values for oxygen and nitrogen. The mean values are: O, $r_a = 1.535$; $r_{Na} = 1.565$; $r_\gamma - r_a = 0.015$. N·O, $r_a = 2.332$; $r_{Na} = 2.495$; $r_\gamma - r_a = 0.072$.

The numbers derived from ethylhydroxylamine are omitted, for the reason stated above. The above refractive power of oxygen is practically identical with that deduced from observations of water and organic compounds containing hydroxyl; the ordinary formula for hydroxylamine is, therefore, confirmed on physical grounds.

J. B. T.

Substituted Hydroxylamines. By C. KJELLIN (*Ber.*, **26**, 2377—2385).—In order to obtain the β -substituted hydroxylamines, none of which have previously been isolated, the author prepared the corresponding nitrogen substituted derivative of metanitrobenzaloxime (syn-) by the action of an alcoholic solution of sodium ethoxide and an alkyl iodide, and, by distillation with steam, separated this from the oxygen substituted ether formed at the same time, the latter being easily volatile; the compound was then decomposed by boiling it with concentrated hydrochloric acid.

β-Ethylhydroxylamine, $\text{NHEt}\cdot\text{OH}$, cannot be prepared from its hydrochloride by the action of potash, and the method employed by de Bruyn for the isolation of hydroxylamine (Abstr., 1892, 402) was therefore used. The hydrochloride of the base, which can only be obtained in the form of a brown oil, is dissolved in a small amount of methylic alcohol, and treated with rather less than the calculated amount of sodium methoxide; as the reaction is accompanied by considerable development of heat, the liquid must be cooled. The sodium chloride which separates is filtered off through an asbestos filter, paper being attacked by the base, and the filtrate distilled under a pressure of 15 mm. Methylic alcohol passes over first, followed by a solution of the base in the alcohol, and then the ethylhydroxylamine begins to sublime in groups of small crystals. This substance, after being pressed on a porous plate, forms colourless, odourless, crystalline plates with a pearly lustre, and melts without decomposition at $59-60^\circ$. The crystals are somewhat indistinct, and could not be measured. It is very readily soluble in water and methylic and ethylic alcohols, less readily in ether, benzene, and light petroleum, in the cold, but dissolves in the last named more readily on heating, and is deposited in long needles on cooling. It deliquesces in the air when exposed in loosely stoppered vessels, but when freely exposed volatilises without previous deliquescence; its vapour combines with hydrogen chloride to form white fumes of the hydrochloride. This base has a strongly alkaline reaction, attacks organic matter very vigorously, and reduces copper and silver salts as strongly as hydroxylamine itself. When pure, it may be preserved for a considerable time, but gradually becomes yellow, and acquires a smell something like that of piperidine. It does not appear to have any of the explosive properties which are characteristic of hydroxylamine. It burns with a faintly luminous flame and without deflagration, and is not decomposed by percussion. Hydriodic acid reduces it to ethylamine. Hydrochloric acid at 300° decomposes it with formation of ammonia, and probably of acetaldehyde, but the latter was not actually found among the products of the reaction. The salts with hydrochloric and sulphuric acids are oils, and could not be obtained in the solid form. The acid *oxalate* crystallises from water in small plates melting at $95-97^\circ$, and is readily soluble in alcohol.

β-Ethylhydroxylamine reacts with 1 mol. of phenylic isocyanate forming a compound, the formula of which is probably



It forms transparent crystals, melts at 98° , decomposes at 145° , and in alcoholic solution gives a dark bluish-violet coloration with ferric chloride. It is not affected by aqueous soda in the cold, but decomposes when heated, symmetrical diphenylcarbamide, aniline, carbonic anhydride, and *β-ethylhydroxylamine* being formed.

β-Methylhydroxylamine is prepared in a manner similar to the ethyl derivative, which it resembles in its general properties. The last portion of the distillate obtained during the preparation is redistilled, and the base then passes over as a colourless liquid, which, when cooled or shaken, solidifies in long, colourless prisms. When rapidly heated in a

wide melting point tube, it melts at 42° , and solidifies again at 20° , but a thermometer immersed in the substance shows a temperature of 36° for the melting point. It deliquesces in the air forming a liquid which rapidly evaporates. Like the ethyl derivative, it has no explosive properties; it is reduced by hydriodic acid to the corresponding amine, and is decomposed by hydrochloric acid. Of the salts, the hydrochloride and zinc chloride compound have been previously described by Dittrich (*Ber.*, 23, 599), and by Crismer (*Abstr.*, 1890, 558). The *sulphate* is an oil, the *oxalate* only crystallises with difficulty, and the tartrate could not be obtained in the solid form. The *picrate* forms small, yellow tablets, melts at $128-130^{\circ}$, and dissolves very readily in water and alcohol. The free base combines with 1 mol. of phenylic isocyanate to form a substance of the formula $\text{NHPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{OH}$; this crystallises from hot light petroleum in small tablets melting at $93-94^{\circ}$ with decomposition. In its chemical properties it resembles the corresponding derivative of the ethyl compound.

Hydroxylamine reacts with 1 mol. of phenylic isocyanate to form a white powder, which is only slightly soluble in the usual solvents, and melts at 144° with decomposition. This substance has a reducing action, gives a bluish-violet coloration with ferric chloride in alcoholic solution, and is not altered by aqueous soda in the cold; on boiling, however, diphenylcarbamide, aniline, carbonic anhydride, and hydroxylamine are formed. It is, therefore, most probably *symmetrical phenylhydroxycarbamide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$. It reacts with a second molecule of phenylic isocyanate to form a substance which melts at 178° with decomposition, and gives a cherry-red coloration with ferric chloride; this substance is probably *diphenylhydroxybiuret*, $\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{OH})\cdot\text{CO}\cdot\text{NHPh}$, and the fact that such a compound is formed from hydroxylamine, but not from ethyl- or methyl-hydroxylamine, is an additional proof that the last two contain the alkyl group combined with the nitrogen atom. A. H.

Thiocarbamides. By H. SALKOWSKI (*Ber.*, 26, 2497—2506; compare *Abstr.*, 1891, 1474).—On heating methylamine thiocyanate, and ethylamine thiocyanate, they are readily converted into the corresponding thiocarbamides, which are extremely soluble; it is for this reason that their formation was not previously observed. The amount of thiocarbamide formed increases as the temperature rises, and is also dependent on the length of time during which the heating is continued. The quantity of bye-products also increases with the temperature. The thiocarbamide was determined by conversion into sulphide; the needful precautions, and the separation of silver sulphide from silver thiocyanate, are fully described. The author replies to Mazzara's recent criticisms (*Abstr.*, 1893, i, 411) on his previous paper; the chief questions at issue are certain discrepancies in the melting points of several compounds. Diethylamine thiocyanate and dimethylamine thiocyanate are converted by heat into the corresponding thiocarbamides; the reaction appears to be independent of the temperature ($130-150^{\circ}$) and of the time; the diethylamine salt undergoes change less readily than the dimethylamine

derivative, but, in both cases, it is much less complete than with the salts of the primary amines. Dimethylthiocarbamide, $\text{NMe}_2\cdot\text{CS}\cdot\text{NH}_2$, is deposited from water in prisms; it melts at 159° , and is not altered on exposure to air. These results are at variance with the observations of Spica and Carrara, who describe this compound as deliquescent, and melting at $81\text{--}82^\circ$. Diisobutylamine thiocyanate and diisobutylamine thiocyanate cannot be converted into the thiocarbamides by heat, as the reaction proceeds with even greater difficulty than in the case of the diethylamine salt.

J. B. T.

Formaldehyde. By G. PULVERMACHER (*Ber.*, **26**, 2360—2363).—With hydrazine hydrate, formaldehyde yields *formalazine*, $\text{C}_2\text{H}_4\text{N}_2$. This is a very insoluble, amorphous substance, readily hydrolysed by mineral acids to formaldehyde and salts of hydrazine. No pure hydrochloride could be isolated, but a *platinochloride*, $(\text{C}_2\text{H}_4\text{N}_2)_6\text{H}_2\text{PtCl}_6$, was prepared. Formalazine is reduced by zinc and acetic acid to ammonia and methylamine; no symmetrical dimethyldiazine could be found among the products.

C. F. B.

Separation of Volatile Fatty Acids. By M. WECHSLER (*Monatsh.*, **14**, 462—469).—Two fatty acids, in molecular proportion, were dissolved in water, neutralised to the extent of four-fifths with soda, the remaining acid distilled over with steam, enough sulphuric acid added to the residue to liberate three-fourths of the combined acids, the liberated acids distilled over, and the remaining acid finally liberated with sulphuric acid, and distilled over. The mixtures investigated were formic and acetic, acetic and propionic, acetic and butyric, acetic and isobutyric, propionic and butyric, butyric and isovaleric, butyric and caproic. The first fraction always contained the acid of greater molecular weight; the last that of less molecular weight; both in a nearly pure condition, except in the case of the mixture of butyric and isovaleric acids, when no separation was effected by the above method.

C. F. B.

Preparation of Silver Formate. By E. J. MAUMENÉ (*Bull. Soc. Chim.*, [3], **9**, 580—584).—When silver nitrate and sodium formate solutions are mixed in equivalent proportions, the precipitate is a double sodium silver formate, and precipitation is gradual and incomplete. In presence of excess of silver nitrate, the double salt is slowly converted into silver formate, but some decomposition takes place at the same time, silver and silver hydride being formed. The author considers that these phenomena could be predicted from his "general laws."

C. H. B.

Preparation of Methylpropionic acid, and Determination of the Solubilities of its Calcium, Barium, and Silver Salts. By V. KULISCH (*Monatsh.*, **14**, 559—571).—This acid is prepared by the interaction of secondary butylic iodide, diethylic malonate, and sodium ethoxide, and subsequent treatment of the resulting secondary diethylic butylmalonate with potash, whereby secondary butylmalonic acid is obtained, crystallising in large plates and melting at 76° . On heating in a reflux apparatus until no more

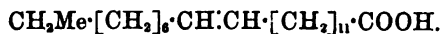
carbonic anhydride is evolved, it yields the acid, $\text{CHMeEt}\cdot\text{CH}\cdot\text{COOH}$, which boils constantly at $196\text{--}198^\circ$. The *calcium salt*, $(\text{C}_8\text{H}_{11}\text{O}_2)_2\text{Ca} + 3\text{H}_2\text{O}$, crystallises in felted masses of prismatic needles, and has the solubility $s = 12.642 + 0.31185(t - 1) - 0.00383(t - 1)^2$. The *barium salt*, $(\text{C}_8\text{H}_{11}\text{O}_2)_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$, crystallises badly. Its solubility is given by the expression $s = 11.711 - 0.33372t + 0.00464t^2$. The *silver salt* is a white, amorphous powder, having the solubility $s = 0.8803 - 0.00287t + 0.000066t^2$.
G. T. M.

Oxidation and Constitution of Erucic acid. By M. FILETI and G. PONZIO (*J. pr. Chem.*, [2], 48, 323—336).—One of the authors has already indicated the results which are obtained by oxidising erucic acid with nitric acid (Abstr., 1893, i, 551). Calcium nonylate crystallises with H_2O , and the magnesium salt with $1\frac{1}{2}\text{H}_2\text{O}$; the cadmium salt melts at $91\text{--}92^\circ$, not 96° .

The nitrogenous compound, previously referred to (*loc. cit.*), is *dinitrononane*, $\text{CH}_2\text{Me}\cdot[\text{CH}_2]_8\cdot\text{CH}(\text{NO}_2)_2$; it is a slightly yellow liquid, which is heavier than water; in the oxidation of erucic acid it is a very minor product, only amounting to some 0.3 per cent. of the erucic acid. The *potassium derivative*, $\text{C}_8\text{H}_{17}\text{KN}_2\text{O}_4$, and the *ammonium derivative* are described.

In order to assure themselves that the non-volatile acid which they obtained along with brassylic acid was arachic acid and not behenic acid, the authors prepared the amide, and compared it with arachamide, which they found to melt at 108° (Scheven and Gössman, *Annalen*, 97, 262, give $98\text{--}99^\circ$); and with *behenamide*, which melts at 84° ; the amide was identical with arachamide. *Brassylamide* melts at 177° .

Thus nonylic and brassylic acids are the chief products of the oxidation of erucic acid by nitric acid, small quantities of dinitrononane and arachic acid being also formed. 1 mol. of erucic acid is thus oxidised to 1 mol. of nonylic and 1 mol. of brassylic acid. This indicates that the double linking in erucic acid occurs between the 13th and 14th carbon atoms from the carboxyl group, giving the formula



Some remarks on Baruch's paper (Abstr., 1893, i, 551) are given in conclusion.
A. G. B.

Oxybehenic acid. By M. FILETI (*J. pr. Chem.*, [2], 48, 336—344).—The method of obtaining this acid has already been indicated (Abstr., 1893, i, 551); it appears to be identical with the acid obtained by Holt and Baruch by the action of strong sulphuric acid on behenolic acid (Abstr., 1893, i, 393), this resemblance being maintained in the derivatives as well as in the acids themselves. The ethylic salt melts at 54° . The author gives several possible formulæ for oxybehenic acid, but he cannot regard the problem of its constitution as solved.
A. G. B.

Lagic acid. By C. BÖRTINGER (*Ber.*, 26, 2327—2329; compare Abstr., 1891, 1061).—The author has failed to obtain crystalline lagic

acid; it may, however, be purified by precipitation with light petroleum from ethereal solution; galic acid is first thrown down, then lagic acid, and finally a colourless, crystalline acid (see below). Lead acetate may be used to approximately separate lagic acid from galic acid, lead galate being first precipitated. *Lead lagate*, $(C_6H_3O_3)_2Pb$, forms a pale yellow, voluminous precipitate which rapidly changes to dense, white crystals on heating. *Aniline lagate* and *dimethylaniline lagate* are not characteristic. With phenylhydrazine, lagic acid yields a compound which, after treatment with ether, forms yellow crystals melting at 108° ; it undergoes decomposition on heating with hydrochloric acid, or acetic acid, phenylhydrazine being eliminated. The *lead salt*, $(C_{10}H_7N_2O_2)_2Pb$, is yellow. The remaining products of the reaction have not yet been fully investigated. Lagic acid is completely decomposed by the action of bromine and water at 100° under pressure, carbonic anhydride, bromoform, and other bromine derivatives of hydrocarbons being formed.

The crystalline acid (see above) was only obtained in very small quantity; it becomes transparent at 171° , sublimes and melts at 178° , and at higher temperatures vapour is evolved which induces tears. It is readily soluble in water, and behaves like lagic acid when treated successively with copper sulphate, ammonia, and acetic acid. The *lead salt* is colourless and crystalline. The *silver salt* readily dissolves in water and ammonia. J. B. T.

Constitution of Dicyanides of Dimolecular Acids. By L. BOUVEAULT (*Bull. Soc. Chim.*, [3], 9, 576—578).—The dicyanides of dimolecular acids (Abstr., 1893, i, 553) in alkaline solution split up into hydrocyanic acid and the acid corresponding with the anhydride from which they were prepared; phenylhydrazine produces a similar decomposition, but with formation of a hydrazide. In presence of concentrated hydrochloric acid, however, the products are a substituted tartronic acid and the acid corresponding to the anhydride. The author considers that these changes can be explained in a similar way to the bipolymerisation of nitriles. Two molecules of the acid cyanide $R \cdot CO \cdot CN + R \cdot CO \cdot CN$ yield the dicyanide $Q-CR \cdot CN$
 $N=C \cdot CO \cdot R$, or, in other words, the cyanides of the dimolecular acids are internal anhydrides of the monoximes of cyanohydroxy- α -diketones $R \cdot CO \cdot C(NO \cdot H) \cdot CR(O \cdot H) \cdot CN$, and it is easy to see that a compound of this type may decompose into an acid of the type $R \cdot COOH$ and a nitrile of a substituted tartronic acid $N \cdot C \cdot CR(O \cdot H) \cdot CN$, the latter immediately undergoing saponification. C. H. B.

Action of Ethylic Bromalkylmalonates on Ethylic Sodiomalonate. By S. RUHEMANN (*Ber.*, 26, 2356—2358).—Ethylic bromomethylmalonate with ethylic sodiomalonate yields, for the most part, dicarbotetracarboxylic acid, the *phenylhydrazide* of which, $C_6(CO \cdot N_2H_5 \cdot Ph)_2$, is a white, crystalline powder decomposing at 255° , and ethylic methylmalonate is also formed. Ethylic bromomethylmalonate exhibits an analogous reaction. C. F. B.

Behaviour of Maleic acid when heated. By Z. H. SKRAUP (*Monatsh.*, 14, 501—504).—Experiments are described which show, in contradiction of Tanatar (Abstr., 1893, i, 193), that inactive malic acid is formed along with fumaric acid (and maleic anhydride) when maleic acid is heated. Beilstein has adopted Tanatar's erroneous statement in the last edition of his *Handbuch*. C. F. B.

Synthesis of Teraconic acid. By H. STORRE (*Ber.*, 26, 2312—2319).—Teraconic acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{COOH})\cdot\text{CMe}_2$, is prepared by the action of sodium ethoxide (2 mols.) on a mixture of diethylic succinate (1 mol.) and acetone (2 mols.) in absolute ether at low temperatures; the product is dissolved in ice-cold water, and the sodium salt decomposed by dilute sulphuric acid; on extraction with ether, a mixture of two acids is obtained, which can be separated by treatment with benzene, in which teraconic acid is insoluble. The teraconic acid was identified by its properties and those of its calcium and barium salts, and also by its conversion into terebic acid. The yield is 55 per cent. of the theoretical. The author considers that the condensation of acetone and diethylic succinate proceeds in a manner similar to that of succinic acid and aldehydes as observed by Fittig and his scholars, and that the formation of teraconic acid is preceded by that of a hypothetical ethylic diaterebate, $\text{COOEt}\cdot\text{CH}_2\cdot\text{CH}(\text{COOEt})\cdot\text{CMe}_2\cdot\text{OH}$. The second acid, which is readily soluble in benzene, is being further investigated. Ethylic succinosuccinate was the only product which could be obtained by the action of sodium, or of sodium ethoxide, on a mixture of ethylic acetate and ethylic succinate. J. B. T.

Action of Sodium Ethoxide on Ethylic Dibromosuccinate. By G. PUM (*Monatsh.*, 14, 491—500; compare Abstr., 1888, 1058).—The product of the action of sodium ethoxide (2 mols.) on ethylic dibromosuccinate (1 mol.), in absolute alcoholic solution, contains 87 per cent. of ethylic ethoxymaleate, the remainder being ethylic acetylenedicarboxylate. By cautiously hydrolysing the product with alcoholic potash and adding the calculated amount of acetic acid and crystallising, potassium hydrogen acetylenedicarboxylate was first obtained, and then *potassium hydrogen ethoxymaleate*, which crystallises in thin plates. The acid itself, $\text{COOH}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{COOH}$, forms minute, white needles which melt at 144—147°.

When the crude product above mentioned is dissolved in chloroform, it takes up bromine, and the quantity of ethylic dibromomaleate isolated from this was such as to show that it had been formed from the ethoxymaleate as well as from the acetylenedicarboxylate.

C. F. B.

Isomerism in the Mucic acid Series. By Z. H. SKRAUP (*Monatsh.*, 14, 470—490).—Ethylic mucate (which melts at 172°, and not at 158° as the text-books assert, and forms a crystalline compound, $\text{COOEt}[\text{CH}\cdot\text{OH}]_2\text{COOEt} + \text{CaCl}_2$, with calcium chloride), when boiled for one hour with acetic chloride, yields *ethylic α-tetracetylmucate*, melting at 189°; if heated for four hours at 100°

with acetic chloride in a sealed tube, it yields an isomeric β -compound which melts at 122° , is much more soluble in acetone than the α -isomeric, and is much more readily hydrolysed by alcoholic soda. The latter can be partially converted into the β -variety by heating it with an acetic acid solution of hydrogen chloride. Both substances are optically inactive, and both yield mucic acid, melting at 225° (the text-books give a wrong melting point), when hydrolysed with mineral acids. The same acid is also obtained, but in small amount, when the hydrolysis is effected by means of alkalis, the main product consisting of a syrupy mixture of two acids identical in composition with mucic acid, and of which the calcium salts are amorphous, and have respectively the composition $C_6H_8O_6Ca + 3H_2O$ and $C_6H_8O_6Ca + 2H_2O$. Alcoholic ammonia attacks both α - and β -tetracetylmucates, the latter the more readily, and among the products mucamide was identified. Benzylamine converts the β -compound into *ethylic tetracetylbenzylmucamate*,



melting at 182 – 184° , and an oil, the latter in larger amount; the α -compound yields a similar oil, but no crystalline compound.

Benzoic chloride, under the same circumstances as acetic chloride, does not form two isomeric derivatives of ethylic mucate; *ethylic di- and tetra-benzoylmucate*, melting respectively at 174° and 124° , are obtained.

Mucic acid itself, when heated with acetic anhydride and a few drops of concentrated sulphuric acid, yields one *tetracetylmucic acid* only; this melts at 242 – 243° , and crystallises with 2 mols. either of water or alcohol. *Monacetylmucic acid* was found in the mother liquors from the preparation of ethylic α - and β -tetracetylmucates; it melts at 198° , and crystallises with $1H_2O$ in white prisms.

C. F. B.

The Thiophen Group. By J. MARCUSSE (Ber., 26, 2457–2465).—The author has been unable to obtain thiophen derivatives having a halogen or nitro-group in the ortho-position to a CO group.

Phenyl thiényl ketone is most easily obtained by exposing a mixture of thiophen, aluminium chloride, and excess of benzoic chloride to direct sunlight. It boils at 300° , and solidifies in needles.

Dibromothiényl phenyl ketone, $C_8SHBr_2\cdot CPh$ [$= 2 : 3 : 5$], is obtained by allowing the ketone to remain for some time in contact with excess of bromine. It crystallises in beautiful white needles, and melts at 80° . The *oxime* forms slender needles, melts at 176° , and is soluble in sodium hydroxide. The oxime is not altered by boiling with concentrated sodium hydroxide, but when warmed with acetic anhydride, it yields an *acetyl compound*, which crystallises in slender needles, and melts at 109° .

Dibromothiényl phenyl ketone is scarcely acted on when allowed to remain with excess of bromine for eight days at the ordinary temperature; when heated at 100° , it yields tetrabromothiophen. When mixed with cold fuming nitric acid, it yields metanitrobenzoic and benzoic acids.

Benzoylethylthiophen, when suspended in bromine water and

treated with bromine at 0° , is completely converted into tetrabromothiophen. A *monobromo-compound*, $C_4SHEtBr \cdot CPh$ [= 2 : 3 : 5], is obtained by shaking benzoylethylthiophen with bromine water and subjecting the product to steam distillation. It is a yellow oil which is converted into tetrabromothiophen by the further action of bromine.

Nitrobenzoylethylthiophen, $COPh \cdot C_4SHEt \cdot NO_2$, is obtained by gradually adding fuming nitric acid to the ketone and cooling with water. It crystallises in pale yellow needles, melts at 117° , and gives a beautiful violet coloration with sodium hydroxide in alcoholic solution. The nitro-group is not eliminated by boiling with hydroxylamine and alcoholic potash.

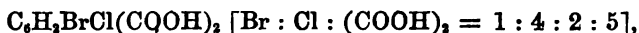
Dibromothiophencarboxylic acid, when heated with excess of bromine in a sealed tube at 100° , is converted into tetrabromothiophen. E. C. R.

Action of Sodium on Orthodibromobenzene. By W. HOSAEUS (*Monatsh.*, 14, 323—332).—Goldschmiedt has shown that by the action of sodium on metadibromobenzene and paradibromobenzene, substances of the formula $C_7H_5Br_2$ are formed (*Monatsh.*, 1886, 541). When orthodibromobenzene, dissolved in ether, is boiled with metallic sodium for about 200 hours, a substance of the same formula is obtained, to which the author gives the name of *orthotridecaphenylene dibromide*. It is a yellow, amorphous powder, which softens at about 245° , and melts at 280 — 290° . Like the isomeric substances obtained by Goldschmiedt, it is insoluble in alcohol, and readily soluble in benzene, chloroform, and carbon bisulphide, but differs from them in being soluble in ether. It was found impossible to obtain any further condensation, either by the action of sodium or heated magnesium on the compound. The molecular weights of all three substances were determined by the boiling-point method, benzene being used as the solvent. In each case the molecular weight was found to correspond with the formula $C_7H_5Br_2$. Schiff's method for the preparation of orthodibromobenzene (*Abstr.*, 1891, 44) was employed, but orthodibromaniline sulphate, instead of the free base, was diazotised in alcoholic solution by means of ethylic nitrite. In this way, a yield of 50 per cent. of the theoretical was obtained. A. H.

Parachlorobromocymene and its Oxidation Products. By G. PLANCHER (*Gazzetta*, 23, ii, 68—75).—On heating parabromothymol with phosphorus pentachloride at 160 — 200° , neutralising with sodium carbonate, and distilling the product in a current of steam, parachlorobromocymene passes over, whilst *tribromothymyl phosphate*, $(C_{10}H_{13}Br)_3PO_4$, remains; the latter can be purified by crystallisation from a mixture of alcohol and ether, and forms opaque, acicular crystals, melting at 94 — 95° .

Parachlorobromocymene is also obtained by brominating, in presence of iodine, the chlorocymene prepared from thymol; it is a colourless, almost odourless, highly refractive liquid, which boils at 259 — 261°

under a pressure of 750·86 mm. On oxidation with dilute nitric acid, it yields *chlorobromoterephthalic acid*,



which is purified by crystallisation from acetic acid; it forms long, lustrous needles, begins to sublime at 240°, and melts at 308—310° (corr.), with slight decomposition. It is soluble in alcohol and acetic acid, but only sparingly in boiling water and benzene; the *diethylic* salt melts at 115—116·5°. The products of oxidation also contain *chlorobromoparatoluic acid*, $\text{C}_6\text{H}_3\text{MeBrCl}\cdot\text{COOH}$ [$\text{Br} : \text{Cl} : \text{Me} : \text{COOH} = 1 : 4 : 2 : 5$], and a *chlorobromocumic acid* (?), which are best separated by distillation in a current of steam; the latter acid forms small prisms melting at 124—128°, but was not obtained in sufficient quantity for complete examination. The former acid separates from acetic acid in small, silky crystals melting at 185—187°; it is soluble in alcohol or acetic acid, but only sparingly so in benzene, petroleum, or water.

W. J. P.

Elimination of Halogens from Substituted Phenols. By F. W. SCHLIEPER (*Ber.*, 26, 2465—2471; compare Abstr., 1892, 704).—*Chlorometanitrophenol* is prepared by passing dry chlorine over finely-divided metanitrophenol; it does not crystallise from the usual solvents, and, after washing with water and drying, melts at 120°. When warmed with stannous chloride (6 mols.) and concentrated hydrochloric acid, it yields *chlorometamidophenol*, which melts at 85—87°.

Chloronitroanisole is prepared by the interaction of chloronitrophenol, sodium methoxide, and methylic iodide. It crystallises in bright yellow needles, melts at 90°, and, on reduction, yields chloranisidine.

Iodometanitrophenol is obtained by adding powdered iodine and mercurous oxide to an acetic acid solution of metanitrophenol. It is a bright yellow powder, melts at 134°, and, on reduction, yields metamidophenol.

Iodonitroanisole, prepared in a similar way to the chlorine compound, crystallises in bright yellow needles, melts at 121—122°, and, on reduction, yields metanisidine, which is an oil, and boils at 250—260° (uncorr.).

Bromorthonitrophenol and bromoparanitrophenol, as stated by Brunek and Körner, on reduction, yield bromorthamido- and bromoparamido-phenol respectively.

When the above chloranisidine is diazotised and the diazo-groups are displaced by hydrogen by Friedländer's method, it yields orthochloranisole, which boils at 198°; from this the author concludes that the above compounds have the constitution $\text{OH} : \text{halogen} : \text{NO}_2 = 1 : 2 : 3$.

E. C. R.

Metanitroorthocresol. By O. MICHEL and E. GRANDMOUGIN (*Ber.*, 26, 2349—2354).—The mixture of nitroindazole and nitrocresol (containing respectively 30 and 70 per cent. of these substances) obtained by diazotising nitrotoluidine and heating the product (Abstr., 1891, 312) is dissolved in very dilute aqueous soda, and the

solution is saturated with carbonic anhydride, which precipitates the nitroindazole. The nitrocresol remains in solution, and can be precipitated by the addition of mineral acids. It was thus obtained pure, and various derivatives of it were prepared; their melting points differ considerably from those of the same substances, as previously prepared from impure materials (Abstr., 1884, 1006).

Metanitroorthocresol [$\text{Me} : \text{OH} : \text{NO}_2 = 1 : 2 : 4$] crystallises in pale yellow needles melting at 118° ; its *acetyl* and *benzoyl* derivatives in lustrous, white needles melting respectively at 74° and 126° . With bromine in acetic acid solution, it yields *dibromonitrocresol*, which crystallises in yellowish needles melting at 115° , and yields an *acetyl derivative* in short, white prisms melting at 127° . By allowing nitrocresol to remain with diazotised nitrotoluidine in cold alkaline solution, *ortho*- and *para*-azonitrotoluenenitrocresol

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Me} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{Me} \cdot (\text{OH}) \cdot \text{NO}_2$, [$\text{Me} : \text{N} \&c. : \text{NO}_2 = 1' : 2' : 4'$]

are obtained, and may be separated by crystallisation from aniline and alcohol, in which the *para*-compound is more soluble. The *ortho*-compound [$\text{Me} : \text{OH} : \text{NO}_2 : \text{N} \&c. = 1 : 2 : 4 : 3$] crystallises in matted, brown needles, melts with decomposition at 250 – 260° , and yields an *acetyl derivative* forming brown needles melting at 205° . The *para*-compound [$1 : 2 : 4 : 5$] crystallises in lustrous, red needles melting at 260 – 270° , and its *acetyl derivative*, in orange-yellow needles melting at 211° .
C. F. B.

Preparation of Parabromothymol. By G. PLANCHER (*Gazzetta*, 23, ii, 76–79).—Parabromothymol is conveniently prepared by the direct bromination of thymol in acetic acid solution; the product solidifies when poured into water, and is then purified by precipitating its solution in soda by sulphuric acid. No other compound could be isolated from the product of bromination.
W. J. P.

Metadiiodoquinone. By F. KEHRMANN and J. MESSINGER (*Ber.*, 26, 2377).—Metadiiodoquinone may be obtained by the oxidation of symmetrical triiodophenol by means of chromic acid. The yield is, however, not so good as that given by Siefert's original method of preparation (*J. pr. Chem.*, [2], 28, 437).
A. H.

Phenylallylcarbinol. By H. FOURNIER (*Bull. Soc. Chim.*, [3], 9, 600–601).—*Phenylallylcarbinol*, $\text{C}_6\text{H}_5 \cdot \text{CHPh} \cdot \text{OH}$, is obtained by the action of allylic iodide on benzaldehyde in presence of zinc turnings and dry ether. It is a colourless, somewhat viscous, and highly-refractive liquid, with a feeble, aromatic odour. It boils at 228 – 229° ; sp. gr. at $18^\circ = 1.004$; refractive index for D at $17^\circ = 1.534$; molecular weight as determined by Raoult's cryometric method, 152 (calc. 148).

When heated with acetic anhydride at 180° for three hours, it yields an *acetate*, $\text{C}_6\text{H}_5 \cdot \text{CHPh} \cdot \text{OAc}$, which is a colourless liquid boiling at 239 – 240° ; sp. gr. at $18^\circ = 1.015$.
C. H. B.

Action of Nascent Bromine on some Benzene Derivatives. By W. VAUBEL (*J. pr. Chem.*, [2], 48, 315–322).—This is a con-

tinuation of the author's work on the subject (compare Abstr., 1893, i, 560). The reactions which have been studied are those between nascent bromine and methylaniline, ethylaniline, acetanilide, acet-orthotoluidide, and acetoparatoluidide, respectively. The influence which the various groups concerned in these compounds exert on the entry of the bromine is considered, and illustrated by drawings which represent the author's conception of the benzene nucleus (Abstr., 1891, 1343).
A. G. B.

Reduction of Dinitro-compounds in Alkaline Solution. By E. LELLMANN and J. HAAS (*Ber.*, 26, 2583—2589).—The behaviour of orthodinitrodibenzylamine and of its phenyl derivative on reduction in alkaline solution has been described (Abstr., 1892, 316, 890; 1893, i, 201). The present experiments deal with the reduction of aliphatic alkyl derivatives of the above-named base.

Orthodinitrodibenzylethylamine, $\text{NEt}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, is obtained by heating on the water bath an alcoholic solution of orthonitrobenzylic chloride with mixed aqueous solutions of ethylamine and soda; the separation of the secondary products and the isolation of the new base is described. It separates from alcohol in large, transparent yellow crystals, melts at 56° , and forms sparingly soluble platino- and auro-chlorides. When reduced with zinc dust and alcoholic soda, *orthodiamidodibenzylethylamine* is obtained; this crystallises in white needles, and melts at 94° . *Orthodiamidoäbenzylmethylamine*, prepared by reducing the dinitro-base (Gabriel and Jansen, Abstr., 1892, 218), melts at 96° . *Orthodinitrodibenzylpropylamine* melts at 31° , and the *diamido*-base at 112° . *Orthodinitrodibenzylisobutylamine* melts at 62° , and the *diamido*-base melts at 132° . *Orthodinitrodibenzylallylamine* melts at 55° , and the *diamido*-base at 104° . *Orthodinitrotribenzylamine* melts at 82° , the *diamido*-base at 143° . A small amount of *orthodinitrodibenzylorthotoluidine* is obtained by heating together alcoholic solutions of orthotoluidine and orthonitrobenzylic chloride; it melts at 205° .
A. R. L.

Oxidation of Pentamidobenzene. By A. W. PALMER and H. S. GRINDLEY (*Ber.*, 26, 2304—2307).—Pentamidobenzene hydrochloride is treated with sodium acetate, and the aqueous solution oxidised for 48 hours by means of a stream of air at the ordinary temperature. The product, which is dark brown and insoluble in the ordinary media, appears to be triamidoquinone or amidodiamidoquinol, $\text{C}_6\text{H}_3\text{N}_5\text{O}_2$; it does not melt, but on heating decomposes with evolution of ammonia, is readily soluble in nitric acid, more sparingly in glacial acetic acid and hydrochloric acid with an amber colour; sulphuric acid produces a mahogany colour; with dilute potash or soda, a blue coloration is obtained, which changes after some time. On heating with hydrochloric acid at 130 — 160° under pressure, although the compound appears to be unaltered, yet one-third of the nitrogen is eliminated as ammonia.

By the action of air on pentamidobenzene hydrochloride in aqueous solution, a compound is formed which contains chlorine, dissolves in

water with a reddish-brown colour, and is precipitated by hydrochloric acid.

Pentamidotoluene hydrochloride, on oxidation in presence of sodium acetate, yields a compound $C_6H_4MeN_5O_2$, which closely resembles the benzene derivative, but is somewhat more soluble. J. B. T.

Organic Salts of Diamidophenol and Triamidophenol. By A. LUMIÈRE and A. SETEWETZ (*Bull. Soc. Chim.*, [3], 9, 595—599).—The oxalate and picrate are the only salts of diamidophenol and organic acids that have any special interest. All the others are very unstable, rapidly turn brown, even when their solutions are concentrated in a vacuum, and cannot be isolated in a crystalline form.

Diamidophenol oxalate, $OH \cdot C_6H_3(NH_2)_2 \cdot H_2C_2O_4$, forms small, white crystals, almost insoluble in cold, but somewhat soluble in hot, water, very slightly soluble in cold alcohol or ether. It dissolves easily in cold solutions of alkalis or inorganic acids and in hot solutions of organic acids. In presence of sodium or potassium hydroxide, the solution rapidly absorbs oxygen from the air, and becomes red; in presence of ammonia, it becomes dark blue, this reaction being very sensitive. The salt dissolves in aqueous solutions of certain salts that have a feeble alkaline reaction, such as sodium sulphite or acetate, and the solutions with sulphite are energetic developers of photographic plates. A 2 per cent. solution of sodium sulphite dissolves 1.5 per cent. of the oxalate, a 10 per cent. solution dissolves 5.5 per cent., and a saturated (17 per cent.) solution dissolves 7 per cent.

Diamidophenol picrate, $OH \cdot C_6H_3(NH_2)_2 \cdot 2C_6H_3N_3O_7$, forms confused, silky, lemon-yellow needles, which alter rapidly in presence of air when moist, but are stable when dry. It melts with decomposition at 120° , is only slightly soluble in cold water, somewhat soluble in alcohol, readily in ether or acetone, but insoluble in benzene. The salt is decomposed by acids, and dissolves in alkalis, the latter solutions absorbing oxygen from the air, and becoming deep red-brown in presence of potash or soda, and deep green in presence of ammonia. At about 120° , it decomposes suddenly with incandescence. Diamidophenol picrate reduces soluble silver salts, but has no special value in photography.

Triamidophenol picrate, $C_6H_2(NH_2)_3 \cdot OH \cdot 3C_6H_3N_3O_7$, forms yellow, silky, confused, acicular crystals, only slightly soluble in cold water, but more so in hot, very soluble in alcohol, and also in ether and acetone, forming green solutions in all cases. It is insoluble in benzene, is decomposed by acids, and is only slightly soluble in alkalis. The salt alters very rapidly if exposed to air whilst moist, and becomes deep olive-green, but is stable when dry. It melts with decomposition at about $96-97^\circ$, and at about $140-150^\circ$ decomposes with incandescence. This salt only very slowly reduces soluble silver salts.

Other salts of triamidophenol are obtained by the action of acids on solutions of the sulphite (*loc. cit.*), but the formate, acetate, oxalate, tartrate, and citrate do not crystallise well, and their solutions alter even when concentrated in a vacuum. C. H. B.

Amido-derivatives of Phloroglucinol. By J. POLLAK (*Monatsh.*, 14, 401—427).—When phloroglucinol is heated with aqueous ethylamine at 110—120° in a sealed tube, *diethylamidohydroxybenzene*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NEt})_2$ [$= 1 : 3 : 5$], is formed; if it is desired to obtain the free base, it is best to allow phloroglucinol to remain for some time in contact with ethylamine at the ordinary temperature and in the absence of air. The base is a crystalline substance melting at 106—108°, and is converted by prolonged boiling with water into phloroglucinol. The *hydrochloride*, $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2\cdot 2\text{HCl}$, crystallises in colourless, transparent, triclinic tables ($a : b : c = 1.03734 : 1.06749$; $\alpha = 92^\circ 31\frac{1}{2}'$, $\beta = 96^\circ 41'$, $\gamma = 93^\circ 34'$) melting with decomposition at 199—201°; the *platinochloride*, $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2\cdot \text{H}_2\text{PtCl}_6 + \text{H}_2\text{O}$, crystallises in yellow, lustrous needles, decomposing above 130°. A *triacetyl derivative*, $\text{OAc}\cdot\text{C}_6\text{H}_3(\text{NEtAc})_2$, was obtained in white, triclinic plates $a : b : c = 1 : 1.0459 : 1.6598$; $\alpha = 79^\circ 53'$, $\beta = 65^\circ 54'$, $\gamma = 112^\circ 7'$; it distils unchanged, and melts at 92—95° when crystallised from benzene, but at 80—85° when crystallised from ether; boiling with water converts it into the *diacetyl derivative*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NEtAc})_2$, which forms lustrous, monoclinic prisms $a : b : c = 0.7764 : 1.03960$; it yields an *ethoxy-derivative*, $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{NEtAc})_2$, melting at 65—67°, and a *dinitroso-derivative*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NEtNO})_2$, crystallising in yellowish-white needles, and melting at 136—138°.

When concentrated ammonia is allowed to remain for 1 to 3 days in contact with phloroglucinol in a sealed tube at the ordinary temperature, *phloramine*, $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, is obtained; it crystallises in white needles, and melts at 146—152°. The *hydrochloride* with H_2O , does not melt below 260°, and yields phloroglucinol on prolonged boiling with water; the *triacetyl derivative* is a white, crystalline powder melting at 119—121°. If phloroglucinol is allowed to remain in contact with concentrated ammonia for 14 days, it is partially converted into 1 : 3 : 5-*diamidohydroxybenzene*,



this crystallises in nearly colourless, lustrous prisms, melts at 168—170°, and yields an *acetyl derivative* melting at 201—204°.

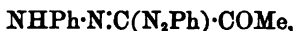
As most of the compounds described decompose in air, especially when still impure, many of the operations were performed in an atmosphere of hydrogen. C. F. B.

Action of Nitrous acid on Amidoparadichlorobenzene. By T. ZETTEL (*Ber.*, 26, 2471—2473).—A compound which the author believes to be *tetrachlorodiazamidobenzene* is obtained by adding amylic nitrite to an alcoholic solution of paradichloraniline. It crystallises from light petroleum in beautiful, lustrous prisms, from benzene in slender needles, melts at 170° with decomposition, and is unaltered by boiling with fuming hydrochloric acid, water, or sulphuric acid. When heated with fuming hydrochloric acid in a sealed tube at 130°, it is converted into dichloraniline and tetrachloroquinol. When reduced with stannous chloride and hydrochloric acid, it yields paradichloraniline and a compound which the author believes to be *paradichlorophenylhydrazine*; this crystallises from hot water in

slender, white needles, melts at 105°, and quickly reduces Fehling's solution. The *hydrochloride* crystallises in slender needles.

E. C. R.

Constitution of the Cyanophenylhydrazines and the Triazole Compounds derived from them. By E. BAMBERGER and P. DE GRUYTER (*Ber.*, 26, 2385—2397).—Formazyl methyl ketone,



is converted by the action of ammonium sulphide into a base melting at 183°, which has been described by Bamberger and Lorenzen (*Abstr.*, 1893, i, 157). A further study of this substance (details of which will shortly be published) has shown that it has the formula $\text{NHPh}\cdot\text{N}:\text{C}(\text{NH}_2)\cdot\text{COMe}$. Substances containing the group



which is analogous to that present in the amidoximes ($\text{OH}\cdot\text{N}:\text{C}\cdot\text{NH}_2$), are termed by the authors *amidrazones*, and the base in question therefore receives the name of *acetylamidrazone*. When treated with acetic anhydride, it is converted into phenylacetylmethyl-

triazole, $\text{NPh}\cdot\text{N}=\text{C}(\text{COMe})\cdot\text{NMe}$, which, on oxidation by potassium permanganate in the presence of sodium carbonate, yields phenylmethyltriazolecarboxylic acid, $\text{NPh}\cdot\text{N}=\text{C}(\text{COOH})\cdot\text{NMe}$. This acid is

identical in every respect with the acid obtained by Bladin (*Abstr.*, 1887, 138) from cyanophenylhydrazine by the action of acetic acid and hydrolysis of the product. Starting from the formula proposed by Bladin for cyanophenylhydrazine, his method of formation leads to a formula for the acid which is different from that which would be assigned to it considering the way in which it is obtained from formazyl methyl ketone, as is shown by a comparison of his formula for methyltriazolecarboxylic

acid, $\text{PhN}^1\cdot\text{C}^2(\text{COOH})=\text{C}^3\text{Me}\cdot\text{N}^4$, with those given above. According to

Bladin, the compound is a 1-phenyl-3-methyl-5-carboxylic acid, whilst, according to the method adopted by the authors, it is a 1-phenyl-5-methyl-3-carboxylic acid.

Similar relations hold with regard to phenyltriazolecarboxylic acid, which has also been prepared by the authors, and found to be identical with that previously obtained by Bladin.

Phenylmethyltriazolecarboxylic acid, when heated at the temperature of its melting point, loses carbonic anhydride, and forms phenylmethyltriazole; the latter was obtained by Bladin as an oil, but the authors have succeeded in preparing it in the form of crystals melting at 191°. An isomeric substance which melts at 86—87°, and is undoubtedly different from the compound obtained by Bladin and the authors, has been prepared by Andreocci (*Abstr.*, 1892, 636) by the action of phenylhydrazine on acetylurethane, a mode of formation which leads to a formula identical with that ascribed by Bladin to the

substance obtained by him. These inconsistencies are removed if the formation of dicyanophenylhydrazine is regarded as analogous to the production of the amidoximes by the action of hydroxylamine on cyanides: $\text{N}:\text{C}:\text{CN} + \text{NH}_2\cdot\text{NHPh} = \text{NHPh}\cdot\text{N}:\text{C}(\text{CN})\cdot\text{NH}_2$. Dicyanophenylhydrazine thus becomes *cyanamidrazone*, and the formation of 1-phenyl-5-methyltriazole-3-carboxylic acid is accounted for without difficulty.

The formula proposed for "dicyanophenylhydrazine" is confirmed by the fact that this substance is formed when "flaveanwasserstoff" is treated with phenylhydrazine in alcoholic solution, hydrogen sulphide being evolved. A portion of the "flaveanwasserstoff" is converted by the sulphuretted hydrogen into "rubeanwasserstoff."

A second compound, formed by the combination of phenylhydrazine with cyanogen, is known, to which Senf (*J. pr. Chem.*, **35**, 535) has given the name cyanophenylhydrazine, and the formula $\text{NH}_2\cdot\text{NPh}\cdot\text{C}(\text{NH})\cdot\text{C}(\text{NH})\cdot\text{NPh}\cdot\text{NH}_2$. This compound has been synthesised by the authors in two different ways, both of which lead to the formula $\text{N}_2\text{HPh}\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{NH}_2)\cdot\text{N}_2\text{HPh}$, according to which it is *diamidrazone*.

1. It is formed when "rubeanwasserstoff" is treated in alcoholic solution with phenylhydrazine, hydrogen sulphide being evolved.

2. The same substance is produced by the action of phenylhydrazine on a solution of cyanamidoxime, $\text{NOH}:\text{C}(\text{NH}_2)\cdot\text{C}(\text{NH}_2):\text{NOH}$, in acetic acid. This reaction is quite analogous to that in which the isonitroso-group of the oximes is replaced by the hydrazone group by the action of phenylhydrazine.

This view of the constitution of the triazole derivatives will of course necessitate a change in the nomenclature of the compounds prepared by Bladin, the nature of which is apparent from a consideration of the formulæ given above (compare this vol., i, 58).

A. H.

Acidyl Derivatives of β -Benzylhydroxylamine. By E. BECKMANN (*Ber.*, **26**, 2631—2634).—*Dibenzoyl- β -benzylhydroxylamine*, $\text{CH}_2\text{Ph}\cdot\text{NBz}\cdot\text{OBz}$ (this vol., i, 27), is prepared by treating β -benzylhydroxylamine with benzoic chloride in presence of aqueous alkali; it crystallises in leaflets, melts at 96—97°, and gives no coloration with ferric chloride. *$\beta\beta$ -Benzoylbenezylhydroxylamine*, $\text{CH}_2\text{Ph}\cdot\text{NBz}\cdot\text{OH}$, is obtained when β -benzylhydroxylamine hydrochloride is treated in ethereal solution with sodium carbonate, the solution dried, and benzoic chloride added; it melts at 106°, and its alcoholic solution gives a red coloration with ferric chloride. *α -Benzoyl- β -benzylhydroxylamine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{OBz}$, is formed as already stated (*Abstr.*, 1893, i, 706), by the action of benzoic chloride on *n*-benzylaldoxime; the hydrochloride melts at 147°.

Diacetyl- β -benzylhydroxylamine, $\text{CH}_2\text{Ph}\cdot\text{NAc}\cdot\text{OAc}$, obtained by boiling β -benzylhydroxylamine hydrochloride with acetic chloride, is an oil; when treated with sodium ethoxide, it yields *$\beta\beta$ -acetylbenzylhydroxylamine*, $\text{CH}_2\text{Ph}\cdot\text{NAc}\cdot\text{OH}$, which melts at 124°. *α -Acetyl- β -benzylhydroxylamine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{OAc}$, is obtained in an analogous manner to the corresponding benzoyl compound; the hydrochloride melts at 102—103°.

When benzoic chloride is added to an ethereal solution of α -benzylhydroxylamine, a compound, probably α -benzyl- β -benzoylhydroxylamine, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{NHBz}$, is formed; it melts at $102\text{--}103^\circ$, and its ethereal solution gives no coloration with ferric chloride. When the last-mentioned compound is boiled with benzoic chloride, a substance melting at $60\text{--}65^\circ$ is obtained; it is probably the *dibenzoyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{NBz}_2$.
A. R. L.

Ethers of Quinoneoxime (Paranitrosophenol). By J. L. BRIDGE (*Annalen*, 277, 79—104).—The author's experiments, a portion of which have already been described (Abstr., 1892, 1456), show that paranitrosophenol is identical with quinoneoxime; the compound is not tautomeric, and the quinoneoxime formula completely explains its reactions.

The *dibromide* of quinonemethoxime (*loc. cit.*),



is colourless, and melts at 123° ; the *dichloride* resembles it, melts at 93° , and, when boiled with dilute alcohol, decomposes into two isomeric chloroquinonemethoximes melting at 123° and 97° . These compounds are also formed by treating chloroquinone with α -methylhydroxylamine hydrochloride; it has yet to be decided which of the two theoretically possible formulæ is to be assigned to each of them. Proof that paranitrosophenol is identical with quinoneoxime is furnished by the fact that the nitroso-compound when heated with acetic anhydride yields quinoneacetoxime (m. p. 107°).

Quinonebenzyloxime, $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{CH}_2\text{Ph}$, is obtained as already described (*loc. cit.*), or by treating quinone in aqueous solution with α -benzylhydroxylamine; it crystallises from light petroleum in yellow tables, and melts at $63\cdot5^\circ$. The *dichloride*,



forms colourless, rhombic tables, melts at 64° , and exhibits great stability towards boiling dilute alcohol; the *dibromide* resembles it, and melts at 68° .

Quinonebenzoyloxime (m. p. $172\text{--}174^\circ$; *loc. cit.*) forms a *dichloride*, $\text{CO} < \begin{array}{c} \text{CH} = \text{CH} \\ \text{CHCl} \cdot \text{CHCl} \end{array} > \text{C:NOBz}$, which crystallises in colourless prisms, melts at 165° , and, when boiled with 50 per cent. alcohol, yields a mixture of two isomeric chloroquinonebenzoyloximes; these melt at 197° and 162° respectively. In order to determine the constitution of these compounds, Kehrman's metachloroquinoneoxime (m. p. 140° ; *Ber.*, 21, 3315) was treated with benzoic chloride; the product was a mixture of the two last-mentioned benzoyl derivatives, thus (according to the author) proving Kehrman's compound to be itself a mixture, and destroying the value of his conclusions (*loc. cit.*).

Quinonebenzoyloxime *dibromide* forms colourless prisms, and melts at $145\text{--}146^\circ$ with decomposition; when boiled with dilute alcohol, it yields two *bromoquinonebenzoyloximes* melting at 158° and 171° respectively.

When quinoneoxime in alcoholic solution is treated with bromine, two, or perhaps three, products are formed. One of them, a *dibromoquinoneoxime*, melts at 170° with decomposition, and the corresponding *benzoyloxime* melts at 191° .

When sodium paranitrosodiphenylamine is treated with benzoic chloride, it yields a benzoyl derivative melting at 156° , and when it is treated with ethylic chlorocarbonate, it yields a carbethoxy-derivative melting at 89° . The constitutions of both these compounds have yet to be determined. A. R. L.

Compounds containing the Group $C_2N_2O_2$. By A. ANGELI (*Gazzetta*, 23, ii, 21—37; compare Abstr., 1893, i, 355).—Dibenzoyl-azoxazole forms small, yellow, orthorhombic crystals, $a : b : c = 0.8218 : 1 : 1.3104$.

On oxidising the dinitroso-derivatives of peroxide of isosafrole or isosapirole, or of their bromo- or nitro-derivatives, with alkaline permanganate, acidifying the solution with sulphuric acid, and repeatedly extracting with ether, an *acid*, having the constitution $\begin{matrix} CMe-C \cdot COOH \\ | \\ N \cdot O \cdot O \cdot N \end{matrix}$,

is ultimately obtained. It separates from benzene in large, colourless, flat, monosymmetric needles which contain solvent of crystallisation, and melt at 47° ; $a : b : c = 1.7392 : 1 : 0.6207$; $\beta = 87^{\circ} 1'$. When crystallised from water, it melts at 62° , and when obtained free from the solvent, it melts at 92° . It is very soluble in water, alcohol, ether, or ethylic acetate, but less so in benzene, chloroform, or light petroleum. The same acid is obtained by oxidising methylsynglyloximecarboxylic acid (Abstr., 1884, 1120; 1892, 1175) with nitric acid (sp. gr. 1.45). The *silver* salt is a white powder which blackens in the air, explodes on percussion, and deflagrates on heating.

W. J. P.

Diisonitrosobromisosafrole. By E. LEVI (*Gazzetta*, 23, ii, 37—42; compare Abstr., 1893, i, 196, 261).—*a*-Diisonitrosobromisosafrole, $CH_2 \cdot O_2 \cdot C_6H_2 \cdot Br \cdot C(NO_2) \cdot CMe \cdot NOH$, is formed on reducing its peroxide with zinc-dust and acetic acid in alcoholic solution; it is eventually obtained in beautiful, colourless, lustrous crystals melting at 186° . When heated above its melting point, it decomposes, so that it could not be converted into the β -isomeride by this means. It is very soluble in alcohol or ethylic acetate, but only sparingly so in benzene or light petroleum. The *diacetyl* derivative forms large, white scales melting at 147° ; it dissolves in the ordinary solvents, and is partially hydrolysed by potash in the cold.

Diisonitrosobromisosafrole anhydride, $O < \begin{matrix} N \cdot C \cdot C_6H_2 \cdot Br \cdot O_2 \cdot CH_2 \\ | \\ N \cdot CMe \end{matrix}$, is obtained by brominating diisonitrososafrole anhydride in acetic acid solution; it melts at 120 — 121° , and is insoluble in potash.

Diisonitrososafrole anhydride, $O < \begin{matrix} N \cdot C \cdot C_6H_2 \cdot (NO_2) \cdot O_2 \cdot CH_2 \\ | \\ N \cdot CMe \end{matrix}$, is prepared by direct nitration; it crystallises in beautiful, lustrous prisms melting at 101 — 102° , and is a very stable substance. W. J. P.

Salicylaldoxime. By E. BECKMANN (*Ber.*, 26, 2621—2631).—Hantzsch has shown that the ortho-substituted aldoximes, which appear to be incapable of intramolecular change into stereoisomerides, have the β - (anti-) configuration.

Action of acetic anhydride, and of acetic chloride, on salicylaldoxime (see Lach, *Abstr.*, 1884, 1154; Claisen and Stock, *Abstr.*, 1891, 451). *Benzoylsalicylonitrile*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$, is obtained by heating salicylaldoxime with benzoic chloride over a free flame; it crystallises in long needles, melts at 105° , and yields salicylonitrile on hydrolysis with alcoholic soda.

Salicylobenzoyloxime, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NOBz}$, is prepared by gently warming, at about 60° , salicylaldoxime with benzoic chloride; it crystallises in needles, and melts at 117° . On treatment with alcoholic soda, salicylaldoxime is regenerated, but when the compound is heated alone, salicylonitrile is formed.

Benzoylsalicylaldoxime, $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NOH}$, is formed by heating benzoylsalicylaldehyde with hydroxylamine; it forms white needles, melts at 130° , and, when heated with benzoic chloride, yields benzoylsalicylonitrile.

Dibenzoylsalicylaldoxime, $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NOBz}$, is obtained by benzoylating salicylaldoxime by the Schotten-Baumann method; it melts at 126° .

When salicylaldoxime is benzylated with sodium ethoxide and benzylic chloride, besides the monobenzoyloxime (m. p. 62 — 63°), the *dibenzyl derivative*, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ is also formed; it melts at 34° . When the monobenzyl derivative is benzoylated, the compound $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NO}\cdot\text{CH}_2\text{Ph}$ is formed; it melts at 47° .

n-Benzylsalicylaldoxime, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH} < \begin{smallmatrix} \text{N}\cdot\text{C}_6\text{H}_5 \\ \text{O} \end{smallmatrix}$, prepared by the condensation of salicylaldehyde and β -benzylhydroxylamine, crystallises in pale yellow needles, and melts at 101 — 102° . When treated in alcoholic solution with benzoic chloride and sodium carbonate, it yields the *benzoyl derivative*, melting at 150° ; when the latter or the *n*-benzylsalicylaldoxime is heated with benzoic chloride, *benzylbenzoylsalicylamide*, $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ is obtained; it crystallises in white needles, melts at 114° , and when treated with sodium ethoxide, yields *benzylsalicylamide*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, melting at 134° . By employing the Schotten-Baumann method for the benzoylation of *n*-benzylsalicylaldoxime, dibenzoyl- β -benzylhydroxylamine (see this vol., i, 24) and salicylaldehyde are obtained. *Acetylbenzylsalicylamide*, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, is obtained by acetylating *n*-benzylsalicylaldoxime; it melts at 102° , and gives benzylsalicylamide when treated with sodium ethoxide.

A. R. L.

Stereoisomerism of the Benzhydroxamic acids. By W. LOSSEN (*Ber.*, 26, 2602—2603).—A contribution to the discussion with Hantzsch and Werner (*Abstr.*, 1893, i, 710).

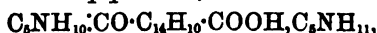
Diphenylmaleic Anhydride. By G. GYSAE (*Ber.*, 26, 2478—2486).—*Ethyl diphenylmaleimide*, $\text{C}_{16}\text{H}_{10}\text{O}_2\cdot\text{NEt}$, is obtained by heating diphenylmaleic anhydride with a solution of ethylamine in dilute

alcohol in a sealed tube at 100°. It crystallises in yellow needles, and melts at 108°. *Methyldiphenylmaleimide*, obtained in a similar way to the ethyl compound, crystallises in bright yellow needles, and melts at 158°.

Diphenylmaleicparabromanil, $C_{16}H_{10}O_2 \cdot NC_6H_4Br$, forms brownish-yellow crystals, and melts at 138°. The author could not obtain the corresponding orthonitro-derivative from orthonitraniline and dimaleic anhydride.

Paratolyldiphenylmaleimide, $C_{16}H_{10}O_2 \cdot NC_7H_7$, forms beautiful brown crystals, and melts at 192°. *β -Nupththyldiphenylmaleimide*, prepared by heating the anhydride, β -naphthylamine, and alcohol at 180°, forms yellowish-grey crystals, and melts at 192°. *Ethylenedidiphenylmaleimide*, $(C_{16}H_{10}O_2 \cdot N)_2C_2H_4$, obtained by heating the anhydride, ethylenediamine, and alcohol at 100°, crystallises in small, bright-yellow plates, melts above 270°, and is extremely insoluble in the ordinary solvents. *Metaphenylenedidiphenylmaleimide* $(C_{16}H_{10}O_2 \cdot N)_2C_6H_4$, is a yellow, crystalline powder, melts at 236°, and is very insoluble.

Piperidodiphenylmaleic piperidine,



is obtained by heating the anhydride with piperidine and alcohol at 100°; it crystallises in white tufts, and melts at 185—186°. When warmed with acetic acid, hydrochloric acid, or sodium hydroxide, it is decomposed into the anhydride and piperidine. Contrary to the statement of Gabriel and Cohn (Abstr., 1892, 178), the author did not obtain a colouring matter from diphenylmaleic anhydride and quinaldine. When the two latter compounds are heated together with a trace of sodium acetate at 200°, a compound of the formula $C_{36}H_{28}N_2O_3$ is obtained; it crystallises from alcohol in beautiful yellow needles, melts at 153°, and has no tinctorial properties.

Metaxylaldiphenylmaleide, $\begin{matrix} CPh:CPh \\ | \\ CO \end{matrix} > C:CH \cdot C_7H_7$, is obtained by heating diphenylmaleic anhydride, metatolylacetic acid, and anhydrous sodium acetate first at 160—180°, and, finally, at 250°. It is an intensely yellow, crystalline powder, and melts at 134°.

Metaxylaldiphenylmaleimidine, $\begin{matrix} CPh:CPh \\ | \\ CO-NH \end{matrix} > C:CH \cdot C_7H_7$, is obtained by heating the preceding compound with alcoholic ammonia at 100°; it crystallises in long, bright yellow needles, and melts at 224—225°. The above maleide also yields a similar compound with ethylamine; it crystallises in slender, pale yellow needles.

Metanitro-xylaldiphenylmaleide, $\begin{matrix} CPh:CPh \\ | \\ CO \end{matrix} > C:C(NO_2) \cdot C_7H_7$, is obtained by treating metaxylaldiphenylmaleide suspended in benzene with a brisk current of nitrous acid (prepared from arsenic trioxide and nitric acid). The solution is allowed to evaporate spontaneously and the product crystallised from a large quantity of cold alcohol. It crystallises in beautiful green tufts, and melts at 165°. When heated in a test-tube, it explodes, the characteristic odour of an isocyanate is observed, and the residue consists of diphenylmaleic

anhydride. The crude substance, which begins to decompose at 110° , partially decomposes when heated with alcohol, with the formation of diphenylmaleic anhydride.

The author was unable to obtain a nitro-compound from metaxylal-diphenylmaleimidine, for oxidation at once takes place, and diphenylmaleinimide is formed.

The author has further examined the behaviour of isatin towards phenylacetic acid, and finds that water is eliminated with the formation of a compound of the formula $N \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}(\text{OH}) \end{smallmatrix} > \text{C}:\text{CPh}\cdot\text{COOH}$, which may be named *isaphenic acid*. It is obtained by heating isatin, phenylacetic acid, and anhydrous sodium acetate at $200\text{--}220^{\circ}$. It crystallises in white leaflets, melts at $294\text{--}296^{\circ}$, is easily soluble in ammonia, dilute sodium hydroxide, and sodium carbonate, and forms well-crystallised lead, ammonium, and silver salts. The *monobromo-derivative*, obtained by treating it with bromine in acetic acid solution, melts above 310° . A *monochloro-derivative* is obtained by warming it with phosphorus trichloride and pentachloride. It crystallises in white leaflets, and melts at 220° .

Hydroisophenic acid, $N \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}(\text{OH}) \end{smallmatrix} > \text{CH}\cdot\text{CH}\cdot\text{COOH}$, is obtained by reducing the acid dissolved in dilute sodium hydroxide with 4 per cent. sodium amalgam. It crystallises in small, white leaflets, melts at 202° , and gives a *silver salt* which separates in white floccs.

E. C. R.

Oxidation products of some Aromatic Thiourethanes. By P. JACOBSON and J. KLEIN (*Ber.*, **26**, 2363—2372).—It was shown some time ago (*Abstr.*, 1886, 700, 876) that phenylthiourethane, when oxidised with alkaline ferricyanide in the cold, yields a bisulphide; when heat is applied, and excess of the oxidising agent used, a thioanhydride is formed. It is now found that, in an analogous fashion, β -naphthylthiourethane yields the *ethyl ether* of a *carbamidothionaphthol*, heat being absorbed in the reaction; and parabromophenylthiourethane, in the cold, yields a bisulphide. Paranitrophenylthiourethane, however, behaves quite differently, and yields paranitrophenylurethane, sulphur being simply replaced by oxygen.

Phenylthiourethane may be readily reduced to bisulphide by treatment with warm alcoholic hydrogen sulphide; hydrogen chloride converts it, in benzene solution, into phenylic cyanate, ethylic chloride, sulphur, and hydrogen sulphide; the last is not evolved, but reduces more thiourethane to bisulphide.

Carbamidothionaphthol ethyl ether, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} > \text{C}\cdot\text{OEt}$, crystallises in yellowish plates, melting at $78\text{--}79^{\circ}$; concentrated hydrochloric acid converts it into *carbamidothionaphthol*, which crystallises in white needles, melts at $235\text{--}236^{\circ}$, and yields a *sodium derivative* as nacreous plates. When carbamidothionaphthol is heated with alcoholic potash, and air is aspirated through the mixture, *diamidinaphthyl bisulphide*, $\text{S}_2(\text{C}_{10}\text{H}_4\cdot\text{NH}_2)_2$, separates in yellowish flakes; its *hydrochloride*, $\text{C}_{20}\text{H}_{16}\text{N}_2\text{S}_2\cdot\text{HCl}$, crystallises in bundles of dark yellow, silky needles.

Paranitrophenylthiourethane is best prepared by the action of thiocarbonyl chloride on paranitraniline; *paranitrophenylthiocarbimide* is formed as an intermediate product, and crystallises in pale yellow needles melting at 112—113°.

Parabromophenylthiourethane bisulphide, $S_2[C(OEt) \cdot N \cdot C_6H_4Br]_2$, crystallises in colourless needles, melting at 86—87°. C. F. B.

Ketones from Acrylic acid. By C. MOUREU (*Bull. Soc. Chim.*, [3], 9, 568—576).—Destructive distillation of calcium acrylate, either alone or mixed with calcium formate, and the action of zinc ethide on acrylic chloride, yield no definite results.

Phenyl vinyl ketone, $COPh \cdot CH:CH_2$, can, however, be obtained by allowing a solution of acrylic chloride in benzene to fall drop by drop into a mixture of aluminium chloride and carbon bisulphide, and separating the products in the usual way by fractional distillation and treatment with sodium hydrogen sulphite. It is very volatile in steam, and crystallises from the aqueous distillate in long needles melting at 42°. It has a persistent aromatic odour, recalling that of cinnamaldehyde, is slightly soluble in water, and dissolves in alcohol, ether, and chloroform. Phenyl vinyl ketone is the simplest of the unsaturated ketones of the benzene series. It combines directly with the theoretical quantity of bromine, but some substitution takes place at the same time. It differs from the saturated ketones of the benzene series in its property of forming a crystalline compound with sodium hydrogen sulphite, but this property is probably connected with the existence of the double bond. With phenylhydrazine, it yields a well-crystallised but very unstable hydrazone, which melts at 130°.

Paraxylyl vinyl ketone, $C_6H_3Me_2 \cdot CO \cdot CH:CH_2$, is obtained in a similar manner by the action of a solution of acrylic chloride in paraxylene on a mixture of aluminium chloride and carbon bisulphide. It boils between 180° and 240° under a pressure of 30 mm., and usually crystallises in the condensing tube. It is insoluble in water, but dissolves in alcohol and ether, and crystallises from the former in slender, brilliant, silky needles melting at 77—78°. Although an unsaturated compound, it combines extremely slowly with sodium hydrogen sulphite. With phenylhydrazine, it yields a hydrazone which crystallises from alcohol, melts at 132—133°, and is very unstable.

Paraxylylethyl paraxylyl ketone, $C_6H_3Me_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_6H_3Me_2$, is formed together with the preceding compound, and in considerably larger proportion. It boils between 255° and 265° under a pressure of 30 mm., and crystallises from alcohol of 80° in slender, brilliant, white needles melting at 52°. It is insoluble in water, but dissolves in alcohol, ether, and benzene. Its molecular weight, as determined by the cryometric method, is 252 (calc. 266). It is a saturated compound, and, with hydroxylamine, yields a well-crystallised oxime, which crystallises from alcohol of 60° in white needles melting at 82—84°.

The formation of paraxylylethyl paraxylyl ketone may be due to the following changes. A portion of the hydrogen chloride, instead of being liberated, unites with the paraxylyl vinyl ketone to form a

compound, such as $C_6H_5Me_2CO \cdot CH_2 \cdot CH_2Cl$, and the latter acts on the excess of paraxylene after the manner of ordinary alkyl chlorides.

C. H. B.

1:3-Diketones. By J. U. NEF (*Annalen*, 277, 59—78).—The author has shown in his researches on ethylic acetoacetate (Abstr., 1892, 140; 1893, i, 628) that the ethereal salts of β -ketonic acids contain the hydroxyl group, and the following experiments furnish evidence that this is also true of the 1:3-diketones (compare, however, Claisen, next abstract).

When sodium benzoylacetone is suspended in ether and treated with acetic chloride, the chief product is a neutral compound, α -benzoyl- β -acetoxypropylene, $CHBz \cdot CMe \cdot OAc$, which boils at 170° (22 mm.) with partial decomposition, and appears to undergo previous conversion into a stereo-isomeride. The other products are α -acetylbenzoyl- β -hydroxypropylene, $CACbz \cdot CMe \cdot OH$, and benzoylacetone; they are separated by fractional treatment with alkali, the former being much more strongly acidic than the latter. It melts at 35° , boils at 167° (22 mm.), and forms a copper salt which crystallises from benzene in greenish-blue needles, and melts at 228° with decomposition. A certain quantity of α -benzoyl- β -acetoxypropylene is formed by heating benzoylacetone with acetic anhydride at 170° , showing that the latter may be regarded as α -benzoyl- β -hydroxypropylene.

By treating sodium benzoylacetone with benzoic chloride there is formed α -dibenzoyl- β -hydroxypropylene, $CBz_2 \cdot CMe \cdot OH$ (Smith, *Inaug. Diss.*, 1889), melting at 115° , together with α -benzoyl- β -benzoxypropylene, $CHBz \cdot CMe \cdot OBz$, a neutral oily compound.

When sodium acetylacetone is treated with benzoic chloride, two acidic compounds, namely, acetylacetone and α -acetyl- β -hydroxypropylene, are formed, and two neutral compounds, namely, α -acetylbenzoyl- β -benzoylpropylene, $CACbz \cdot CMe \cdot OBz$, melting at 103° , and an oil, perhaps, $CHAc \cdot CMe \cdot OBz$.

α -Diacetyl- β -hydroxypropylene, $CAC_2 \cdot CMe \cdot OH$, an acidic compound boiling at 104° (19 mm.), is obtained, together with a neutral substance, by treating sodium acetylacetone with acetic chloride.

Dry silver acetylacetone reacts with ethylic iodide, forming α -ethylacetylacetone, $CEtAc \cdot CMe \cdot OH$ (Combes, *Ann. Chim. Phys.*, [6], 12, 247), and a neutral compound, $CHAc \cdot CMe \cdot OEt$, which boils at 175 — 180° .

A. R. L.

1:3-Diketones. By L. CLAISEN and others (*Annalen*, 277, 162—206; compare Nef, preceding abstract).—The author criticises Nef's views on the constitution of ethylic acetoacetate, and also the nomenclature employed by the latter. He thinks that the constitution of the ethylic salt itself and of its metallic derivatives are distinct problems. The conversion of so small a quantity as one-tenth of ethylic acetoacetate, by treatment with acetic anhydride, into an acetyl derivative (Nef), is an argument against rather than in favour of the hydroxyl formula.

The constitution of ethylic diacetoacetate (ethylic acetylacetone-carboxylate), from acetic chloride and ethylic sodacetoacetate,

has been determined by Perkin (Trans., 1892, 823, 854). Its alcoholic solution gives a dark red coloration with ferric chloride; the copper salt, $(C_8H_{11}O_4)_2Cu + 2H_2O$, melts at 151° . When ethylic diacetoacetate is heated with hydroxylamine hydrochloride, it gives ethylic α - γ -dimethylisooxazole- β -carboxylate, $COOEt:C \begin{smallmatrix} \nearrow CMe \cdot N \\ \searrow CMe \cdot O \end{smallmatrix}$, which boils at 218 — 220° ; the corresponding acid melts at 142° . Methyllic diacetoacetate melts at 22 — 23° , and boils at 196 — 198° .

Ethylic acetylacetone carbonate, $CHAc:CMcO \cdot COOEt$, is obtained together with ethylic acetylacetonecarboxylate by treating an alkali (preferably the potassium) derivative of acetylacetone with ethylic chlorocarbonate; it is a colourless oil, boils at 124 — 126° (18 mm.), or at 221 — 224° (ordinary pressure), with partial decomposition; its sp. gr. is 1.082 at 15° .

When the alkali derivatives of benzoylacetone are suspended in ether and treated with benzoic chloride, benzoylacetone, dibenzoylacetone, $C_{17}H_{14}O_3$, and tribenzoylacetone are formed. The dibenzoylacetone is strongly acid, and is extracted from the product by sodium carbonate solution; it melts at 101 — 102° , and gives a blue precipitate with copper acetate solution. The ferric salt, $(C_{17}H_{12}O_3)_3Fe + 3H_2O$, is a yellowish-red, crystalline powder. When heated with aqueous alkalis, the dibenzoylacetone decomposes into dibenzoylmethane (m. p. 80 — 81°) and acetic acid; and if it is dissolved in hot alcohol and allowed to slowly crystallise, an isomeride is obtained which melts, when rapidly heated, at 109 — 112° , and gives no precipitate with copper acetate solution.

Benzoic chloride reacts with the alkali derivatives of acetylacetone forming acetylbenzoylacetone, $CHAc:Bz$, which melts at 34 — 35° , and forms a copper salt, melting at 224 — 225° ; and dibenzoylacetylacetone, $CACBz:CMc \cdot OBz$, melting at 102 — 103° . A. R. L.

Nitration of Orthiodobenzoic and Orthiodosobenzoic acids. By H. GÜMBEL (Ber., 26, 2473—2475).—Iodosobenzoic acid is obtained by the action of a mixture of fuming nitric acid (1 part) and concentrated sulphuric acid (3 parts) on orthiodobenzoic acid at ordinary temperatures. If, however, orthiodobenzoic acid is heated with 20 times its weight of the acid mixture at 170 — 175° for 4—5 hours, it yields an acid of the formula $NO_2 \cdot C_6H_4I \cdot COOH$, which crystallises in long, lustrous, colourless needles, and melts at 192° (uncorr.). When the iodobenzoic acid is heated with the acid mixture at 135 — 140° for three hours, it yields the acid $NO_2 \cdot C_6H_4(10) \cdot COOH$, which crystallises in slender, white needles, and decomposes about 194 — 196° . When treated with potassium iodide, it is completely converted into nitro-orthoiodobenzoic acid, and conversely it may be obtained from the latter by oxidation with potassium permanganate.

When orthiodobenzoic acid is heated with the acid mixture at 220 — 230° , iodine vapours are formed, but no definite compounds could be isolated.

E. C. R.

Condensation of Aromatic Aldehydes with Cyanacetic acid. By E. FIQUET (Ann. Chim. Phys., [6], 29, 433—504).—Cyanacetic

acid is best prepared by gradually adding pulverised potassium cyanide to a solution of chloracetic acid in water (2 parts) heated on a water bath, and treating the product cautiously at 0° with hydrochloric acid; the author is unable to verify the melting point (80°) recorded by Van't Hoff, but finds that the acid melts at $69-70^{\circ}$.

Aromatic aldehydes react with cyanacetic acid, forming compounds of the type $\text{CHR}^{\cdot}\text{C}(\text{CN})\cdot\text{COOH}$, R^{\cdot} being an aromatic alkyl. The production of α -cyanocinnamic acid from benzaldehyde and cyanacetic acid has already been described (Abstr., 1892, 1340); this acid, if heated with aqueous potash, decomposes into malonic and benzoic acids, whilst if heated with water at $170-180^{\circ}$, benzaldehyde and cyanacetic acid are regenerated. The *sodium*, *silver*, and *copper* salts are described; the *methyl*ic salt crystallises in clinorhombic, tabular prisms, $a : b : c = 1.5023 : 1 : 2.3610$; angle of prism = $98^{\circ} 37'$. The ethylic and other salts have been described by Carrick (Abstr., 1892, 1086). If the ethylic salt is treated with gaseous ammonia in alcoholic solution, a crystalline compound,



is formed, which melts at 187° , and decomposes into benzaldehyde and ammonium malonate when heated with water at $180-200^{\circ}$; it is, therefore, isomeric with the compound described by Carrick (*loc. cit.*). Paranitrobenzoic acid is formed by treating α -cyanocinnamic acid with fuming nitric acid. Continued heating of α -cyanocinnamic acid on the water bath with phosphorus pentachloride gives rise to the formation of *benzylideneacetic chloride*, a compound which is converted by water into α -cyanocinnamic acid, and by alcohol into the ethylic salt of the same acid. Cinnamonitrile, obtained by heating α -cyanocinnamic acid above its melting point, boils at $254-256^{\circ}$, and its sp. gr. at $0^{\circ}/0^{\circ}$ is 1.037. If the nitrile is boiled with hydrochloric acid or potash, cinnamic acid is formed, and, when it is treated with hydrogen sulphide in alcoholic solution, it yields a yellow, crystalline compound, $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{NH}_2$, melting at 112° ; it combines with bromine, forming *phenyldibromopropionitrile*, which decomposes when distilled.

The three toluic aldehydes were prepared by a modification of Etard's method, which is described. *Metamethyl- α -cyanocinnamic acid*, $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{COOH}$, obtained by heating metatoluic aldehyde with cyanacetic acid at $150-160^{\circ}$, is a white, crystalline compound, melts at 156° , is insoluble in water, and devoid of odour; when heated with potash, metatoluic acid is formed. The *methyl*ic salt melts at 95° , and the *ethylic* salt at 85° . *Metamethylcinnamonitrile* passes over at 170° , when the last described acid is distilled under a pressure of 30 mm.; it has an aromatic odour, its sp. gr. at $0^{\circ}/0^{\circ}$ is 1.038, and it is converted into metamethylcinnamic acid when heated on the water bath with potash.

Paramethyl- α -cyanocinnamic acid, from paratoluic aldehyde, melts at 214° , and is less soluble in alcohol and benzene than the last described isomeride; the *methyl*ic salt melts at $110-112^{\circ}$, and the *ethylic* salt at 94° . When the acid is distilled under diminished pressure, *paramethylcinnamonitrile* passes over; it is a crystalline solid, melts at $79-80^{\circ}$, and gives paramethylcinnamic acid when heated with

potash. *Orthomethyl- α -cyanocinnamic acid* melts at 202° , the *methyl*ic salt at $89-90^{\circ}$, and the *ethyl*ic salt at 60° . When the acid is distilled, it decomposes into a compound which yields orthomethylcinnamic acid on treatment with potash.

Paranitro- α -cyanocinnamic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{COOH}$, is obtained by heating paranitrobenzaldehyde with cyanacetic acid at $160-170^{\circ}$; it forms white laminæ, and melts at 208° ; the *ethyl*ic salt melts at $169-170^{\circ}$. *Orthonitro- α -cyanocinnamic acid* melts at $226-228^{\circ}$, and *metanitro- α -cyanocinnamic acid* at $214-216^{\circ}$.

Cinnamyl- α -cyanoacrylic acid, $\text{CHPh}\cdot\text{CH}:\text{CH}:\text{C}(\text{CN})\cdot\text{COOH}$, obtained by heating cinnamaldehyde with cyanacetic acid, forms small, yellow crystals, and melts at 212° ; it yields cinnamic acid when treated with potash, and paranitrobenzoic acid on treatment with fuming nitric acid. The *silver* and *calcium* salts are both amorphous; the *methyl*ic salt melts at 145° , and the *ethyl*ic salt at $118-120^{\circ}$. *Cinnamylacrylonitrile* passes over at 159° , when the acid is distilled under a pressure of 285 mm.; it is a colourless liquid of sp. gr. $0^{\circ}/0^{\circ} = 1.037$, having an odour resembling that of cinnamonnitrile, and combines with four equivalents of bromine. When the nitrile is heated with potash, *cinnamylacrylic acid* melting at $165-166^{\circ}$ is formed.

A. R. L.

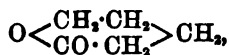
Dry Distillation of Calcium Veratrate. By W. HEINISCH (*Monatsh.*, 14, 455-461).—The distillate contains methyl veratrate and veratrol together with small quantities of guaiacol and veratric acid; the residue contains a small quantity of catechol. These results should be compared with those obtained by other observers in the case of calcium anisate (*Abstr.*, 1882, 616) and dimethyl-*a*-resorcyate (*Abstr.*, 1888, 148).

C. F. B.

Synthesis of β -Pipicoline and Preparation of δ -Valerolactone. By R. FUNK (*Ber.*, 26, 2568-2576).—The method employed by Gabriel (*Abstr.*, 1892, 717) for the synthesis of piperidine is applied by the author to the synthetical production of β -pipicoline. *Ethyl*ic γ -phenoxypropylisuccinate, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}(\text{COOEt})_2$, may be prepared by the action of γ -chloropropyl phenyl ether on ethyl sodium-isosuccinate, or by that of methyl iodide on ethyl sodium- γ -phenoxypropylmalonate; it boils at $268-270^{\circ}$ under 130 mm. pressure. *Ethyl*ic γ -phenoxypropylmalonate can only be distilled without decomposition under diminished pressure; it boils at $265-266^{\circ}$ under 140 mm. pressure; it forms large, rhombic tablets which melt at 32° . γ -Phenoxypropylisuccinic acid, obtained by hydrolysis of the ethyl salt, crystallises from water in colourless plates, and melts with decomposition at 118° . The *silver* salt forms microscopic needles. When the acid is heated, carbonic anhydride is evolved, and *α -methyl- δ -phenoxyvaleric acid*, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{COOH}$, formed; this distils at 327° , and, when cooled, solidifies in crystals which melt at 36° , and are very soluble in alcohol and other solvents. The *nitrile* of this acid is prepared by the distillation of the acid with lead thiocyanate, and is a yellow oil, which boils at about 300° . The reduction of the nitrile by the action of sodium on its alcoholic solution yields *β -methyl- ϵ -phenoxyamylamine*, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}_2$, as an oil

which absorbs carbonic anhydride from the air with great rapidity. The *hydrochloride* forms small, hygroscopic needles, and melts at 88° ; the *picrate* melts at $106-110^{\circ}$, and the *platinochloride* crystallises in yellow needles. When the base is heated with fuming hydrochloric acid at 180° , it is converted into the very hygroscopic *hydrochloride* of β -methyl- α -chloramylamine, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}_2$. The *picrate* of this base crystallises from water in small needles melting at $65-66^{\circ}$, and the *platinochloride* forms sparingly-soluble small, yellow plates. When the hydrochloride is heated with aqueous potash, β -pipecoline (β -methylpiperidine) is formed. The base thus obtained is identical with that prepared by Hessekiel (*Ber.*, 18, 910).

Henry (*Bull. Soc. Chim.*, 45, 341) has shown that γ -chlorobutyric acid loses hydrogen chloride when distilled, butyrolactone being produced. In order to ascertain whether δ -chlorovaleric acid behaves in a similar manner, the author prepared this substance by heating δ -phenoxyvaleric acid (Gabriel, *Abstr.*, 1892, 717) with fuming hydrochloric acid at 180° . The acid forms a brown oil, which solidifies in a freezing mixture, and melts at about 4° . When it is boiled in a flask, hydrogen chloride is evolved and δ -valerolactone,



is formed as a liquid boiling under the atmospheric pressure at about 230° . It is soluble in water, alcohol, and ether, and, when treated with alkalis, yields salts of the hydroxy-acid.

The compound obtained by Weidel (*Abstr.*, 1891, 733), which he terms δ -valerolactone, is different from this substance, since it boils at $222-226^{\circ}$ at a pressure of 56 mm. A. H.

Derivatives of Triacetylgallic acid. By H. SCHIFF (*Annalen*, 277, 206—208).—The melting point of triacetylgallanilide was erroneously printed $101-102^{\circ}$ in a former paper (*Abstr.*, 1893, i, 167); it should be $161-162^{\circ}$, as since shown by Cazeneuve. Triacetylgallacetamide melts at 163° , as stated by Marx (*Abstr.*, 1891, 1220).

A. R. L.

Ethylic Opiante. By R. WEGSCHEIDER (*Monatsh.*, 14, 311—314; compare *Abstr.*, 1892, 1208).—The ethylic opiate melting at 92° , already known, is a pseudo-salt. The normal salt may be prepared by the action of ethylic iodide on silver opiate and of ethylic alcohol on opianic chloride. The new salt is readily soluble in alcohol, &c., sparingly in water, and does not easily crystallise. It melts at $63.5-64.5^{\circ}$. Both this salt and the normal methylic salt are distinguished from the corresponding pseudo-salts by the fact that they are exceedingly difficult to burn in a combustion tube (compare Claisen, *Ber.*, 25, 1768). A. H.

Dependence of Chemical Reaction on the Presence of Water. By R. OTTO (*Ber.*, 26, 2050—2053).—In connection with Baker's recent work on the influence of water on chemical changes (*Proc.*, 1893, 129), the author observes that a number of organic substances, such as benzenesulphonic chloride, phenylic disulphoxide, phenylic bisulphide, paratoluenesulphonic chloride, and benzenesulph-

inic acid, whilst readily reduced by nascent hydrogen in presence of water, are not attacked if water be excluded. W. J. P.

Action of Sulphurous Anhydride on Sodium Phenoxide. By C. SCHALL (*J. pr. Chem.*, [2], 48, 241—253).—When sulphurous anhydride is passed over sodium phenoxide at the ordinary temperature, the product is not the analogue of Kolbe's sodium phenylcarbonate, but the phenyl salt of sodiumsulphonic acid.

Phenylic sodiumsulphonate, $\text{NaSO}_3\cdot\text{OPh}$, is a yellowish-white, light, hygroscopic powder; it is almost insoluble in alcohol, and is slowly decomposed by water with formation of phenol and sodium hydrogen sulphite. When heated with methylic iodide under pressure, it yields *phenylic methanesulphonate*, $\text{CH}_3\cdot\text{SO}_3\cdot\text{OPh}$, together with some anisöl. This crystallises in laminæ or needles, melts at $61-62^\circ$, boils at 279° (uncorr.), and may be sublimed; it dissolves sparingly in cold light petroleum and in water, but freely in other solvents, including strong sulphuric acid.

Parabromophenylic methanesulphonate, $\text{CH}_3\cdot\text{SO}_3\cdot\text{OC}_6\text{H}_4\text{Br}$, obtained by brominating the phenylic salt, crystallises in prisms, and melts at 83° ; it dissolves freely in ether, benzene, and chloroform, but sparingly in alcohol; it is volatile with steam. By hydrolysis, it yields parabromophenol. The corresponding *tetrabromo-derivative* (probably $\text{Br}_4 = 2 : 3 : 4 : 5$) is prepared by heating the bromo-derivative with bromine and fused aluminium bromide; it crystallises in white, silky needles, melts at $164-165^\circ$, and dissolves freely in cold benzene and in warm alcohol and carbon bisulphide; the tetrabromophenol which it yields on hydrolysis melts at $128-129^\circ$. By increasing the proportion of bromine and aluminium bromide, the *pentabromo-derivative* is obtained; this crystallises in white needles, and melts at 171° .

Paranitrophenylic methanesulphonate, $\text{CH}_3\cdot\text{SO}_3\cdot\text{OC}_6\text{H}_4\cdot\text{NO}_2$, is the product of the nitration of phenylic methanesulphonate; it melts at $94-95^\circ$, and dissolves in ether, alcohol, benzene, and glacial acetic acid. The corresponding *amido-derivative* crystallises in white needles, melts at $89-90^\circ$, and dissolves in alcohol and in ether. The *acetamido-derivative* crystallises in needles, and melts at $177-178^\circ$.

Dinitrophenylic methanesulphonate [$(\text{NO}_2)_2 = 2 : 4$] is formed when the nitration of the phenylic salt is conducted with an excess of nitric acid; it crystallises in laminæ, and melts at $82-84^\circ$. The corresponding *diamido-derivative* forms needles which melt with slight blackening at $103-104^\circ$, and dissolve in warm benzene, chloroform, and alcohol. The *diacetyldiamido-derivative* forms felted needles, and melts with slight blackening at $236-237^\circ$.

Phenylic ethanesulphonate, $\text{CH}_3\text{Me}\cdot\text{SO}_3\cdot\text{OPh}$, is obtained, together with some phenetol, when phenylic sodiumsulphonate is heated with ethylic iodide; it crystallises in white laminæ, melts at $34-35^\circ$, boils at $287-288^\circ$, and dissolves easily in benzene and in alcohol. Hydrolysis converts it into ethanesulphonic acid and phenol.

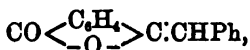
Phenylic α -propanesulphonate, $\text{CH}_3\text{Et}\cdot\text{SO}_3\cdot\text{OPh}$, from phenylic sodiumsulphonate and α -propylic iodide, is a brown, uncrystallisable, sparingly soluble, viscid oil.

Paracresylic sodiumsulphonate, $\text{NaSO}_3 \cdot \text{OC}_6\text{H}_4\text{Me}$, is prepared from sodium paracresoxide in a manner similar to that described above for the preparation of the phenylic compound. *Paracresylic methanesulphonate* crystallises in white cubes, melts at $44.5-46^\circ$, and boils with slight decomposition at 295° (uncorr.), and undecomposed at $260-264^\circ$ under a pressure of 207 mm.; it is volatile with steam, and sublimes; alcohol dissolves it freely; oxidation converts it into *paracarboxylphenylic methanesulphonate*, $\text{CH}_3\text{SO}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, which forms white needles, melts at 224° , and dissolves freely in ether and warm alcohol.

α - and β -Naphthylic sodiumsulphonates, $\text{NaSO}_3 \cdot \text{OC}_{10}\text{H}_7$, were also prepared. A. G. B.

Action of Phosphorus Pentachloride on Benzoicsulphinide. By I. REMSEN (*Ber.*, 26, 2634-2635).—The author points out that Jesurin (*Abstr.*, 1893, i, 715) has overlooked the work of Remsen and Dohme (*Abstr.*, 1889, 992), which contains much of the matter published as new by Jesurin. In conjunction with certain of his students, the author has found that the chloride of benzoicsulphinide consists of two isomeric compounds of melting points 78° and 22° respectively; both are converted by ammonia into benzoic sulphinide. A full description of these and other experiments with parachlorocyanobenzene will appear later in the *American Chemical Journal*. A. R. L.

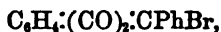
Intramolecular Change of Phthalides into Derivatives of α -Diketohydrindene. By F. NATHANSON (*Ber.*, 26, 2576-2582; compare *Abstr.*, 1893, i, 346).—When a solution of sodium in methylic alcohol is added to one of benzalphthalide,



in the same solvent, the colourless liquid becomes dark red, and a mass of crystals separates, consisting of the sodium compound of β -phenyl- α -diketohydrindene, $\text{C}_6\text{H}_4 : (\text{CO})_2 : \text{CHPh}$. The same result is obtained when ethylic alcohol is used, but if even a small amount of water is present, the yield is no longer quantitative, and deoxybenzoincarboxylic acid, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2\text{Ph}$, is produced. Phenyl-diketohydrindene is also formed when benzalphthalide is boiled with alcoholic potash, or when the methylic salt of deoxybenzoincarboxylic acid is hydrolysed with alcoholic potash. Phenyl-diketohydrindene crystallises in white, nacreous plates melting at 145° . It is insoluble in water, but dissolves readily in other solvents, forming yellow or red solutions; it yields a blue solution with concentrated sulphuric acid; it is a strong acid, and forms a number of coloured salts. Attempts to reduce it to phenylhydrindene proved unsuccessful. *Phenyl-diketohydrindenephénylhydrazone* crystallises in fine, yellow, matted needles melting at $170-174^\circ$. The *dioxime* forms small, white needles melting at $193-196^\circ$. *Phenylmethyldiketohydrindene*, $\text{C}_6\text{H}_4 : (\text{CO})_2 : \text{CMePh}$, is prepared by the action of methylic iodide on the sodium compound, and forms colourless, cubic crystals

melting at 154—155°. The corresponding *ethyl* compound melts at 103—105°.

Ethyl phenyldiketohydrindeneacetate, $C_6H_4:(CO)_2:CPh \cdot CH_2 \cdot COOEt$, is obtained by the action of ethyl chloracetate on the sodium compound, and melts at 104°. *Phenylbromodiketohydrindene*,



is obtained by the direct action of bromine, and crystallises from benzene in white needles melting at 105°. It has no acid properties. The *chloro*-derivative is formed by treating the diketo-compound with phosphorus pentachloride, and crystallises in yellow needles melting at 114—116°. The halogen atom of these compounds is not removed by boiling with alcoholic ammonia or potassium cyanide, but readily reacts with aniline, forming an *anilido*-derivative, $C_6H_4:(CO)_2:CPh \cdot NHPh$, which melts at 210—211°. *Bisphenyldiketohydrindene*, $C_6H_4:(CO)_2:CPh \cdot CPh:(CO)_2:C_6H_4$, is produced by the oxidation of the diketohydrindene by means of nitrous acid. It crystallises in white, lancet-shaped needles melting at 208°. *Dinitrophenyldiketohydrindene* is obtained by the direct action of fuming nitric acid, and melts at 128—131°.

Ethylidenephthalide, when treated with sodium methoxide, is converted into β -methyldiketohydrindene, identical with that described by Wislicenus (Abstr., 1889, 1067).

Ethinediphtalide is converted in a similar manner into *bisdiketohydrindene*, $C_6H_4:(CO)_2:CH \cdot CH:(CO)_2:C_6H_4$; this crystallises from hot nitrobenzene in long, violet needles which do not melt below 350°. It is insoluble in solvents of low boiling point, but dissolves in alkalis, forming violet solutions from which it is precipitated unchanged by acids.

A. H.

Diphenyl Group. By R. LOEWENHERZ (*Ber.*, 26, 2486—2487).—The diphenyltetracarboxylic acid obtained by the author (Abstr., 1892, 1464) by the oxidation of ditolyldicarboxylic acid with potassium permanganate corresponds with phthalic acid, and the author therefore names it *diphthalic acid*. It is less soluble in water than phthalic acid, crystallises in colourless needles, and does not melt at 250°. When heated with resorcinol, it yields a *disfluorescein*, which is very similar to fluorescein, exhibits a somewhat stronger fluorescence, and is converted by bromine into a *dis eosin*. The latter closely resembles eosin, and gives almost the same shades on wool.

A *dihelianthin* is obtained by combining diazotised benzidine-disulphonic acid with dimethylaniline; it is very similar to dimethyl-orange. The corresponding *diethyl* compound obtained from benzidine-disulphonic acid and diethylaniline is very similar to diethyl-orange.

E. C. R.

Alkyl Derivatives of Benzoin. By E. FISCHER (*Ber.*, 26, 2412—2415).—When a methyl alcoholic solution of benzoin is saturated with gaseous hydrogen chloride at 30—40°, and then allowed to remain at the ordinary temperature, *methylbenzoin*, $CPhO \cdot CHPh \cdot OMe$, is formed, and may be obtained crystallised in white needles which melt at 49—50° (corr.). It is oxidised by nitric

acid to benzile, yields an oily product with phenylhydrazine, and, with hydroxylamine, yields *methylbenzoinoxime*, $\text{NOH}:\text{CPh}:\text{CHPh}:\text{OMe}$, crystallising in small needles, and melting at $130-132^\circ$ (uncorr.).

Ethylbenzoïn, $\text{CPhO}:\text{CHPh}:\text{OEt}$, resembles the methyl compound; it melts at 62° (corr.), and yields compounds with phenylhydrazine and hydroxylamine, but they have not been obtained crystallised.

C. F. B.

Anilides of Benzoïn and Benzile. By B. LACHOWICZ (*Monatsh.*, 14, 279—293).—In this investigation, special care was taken to vary the methods and conditions of preparation, in order to ascertain whether any of the mono- or di-anilides occurred in two isomeric forms; this was in no instance found to be the case.

Benzoïn-anil, $\text{NPh}:\text{CPh}:\text{CHPh}:\text{OH}$, has been prepared by Voigt (*J. pr. Chem.*, 34, 2). It combines with 1 mol. of hydrogen chloride to form a *hydrochloride*, which crystallises from hot alcohol in short, colourless needles melting at 185° . *Benzoïn-anil-anilide*, $\text{NPh}:\text{CPh}:\text{CHPh}:\text{NHPh}$, is not formed by the action of aniline on benzoïn even at 240° , but may be obtained when aniline hydrochloride is heated with benzoïn at 160° . It crystallises from alcohol in colourless needles melting at 125° . This substance is not acted on by boiling alcoholic potash or hydrochloric acid, but is converted by nitrous acid into a yellow, unstable nitroso-compound. *Benziledianil*, $\text{NPh}:\text{CPh}:\text{CPh}:\text{NPh}$, which has been previously prepared by Siegfeld (*Ber.*, 25, 2601), is also formed when benzoïn-anil is heated in the air with aniline, the atmospheric oxygen taking part in the reaction. It is decomposed by hydrochloric acid, but not by alcoholic potash. On treatment with phenylhydrazine hydrochloride, it is converted into benzilediphenylhydrazine. *Benzoïn-anil-paratoluidide*, $\text{NPh}:\text{CPh}:\text{CHPh}:\text{NH}:\text{C}_6\text{H}_4$, is obtained by heating together benzoïn-anil and paratoluidine hydrochloride. It forms colourless prisms, and melts at 139° . On repeated recrystallisation from dilute alcohol, it is converted into a mixture of benzoïn-anil-anilide and benzoïn-toluidide. *Benzileanil-paratoluidil*, $\text{NPh}:\text{CPh}:\text{CPh}:\text{N}:\text{C}_6\text{H}_4$, is prepared by heating benzoïn-anil with paratoluidine in an open vessel, and forms flat, yellow needles melting at 135° . On treatment with hydroxylamine hydrochloride, it yields benzileoximeparatoluidil (*Abstr.*, 1892, 1470). *Benzoïn-paratoluidil-paratoluidide*, $\text{C}_6\text{H}_4:\text{N}:\text{CPh}:\text{CHPh}:\text{NH}:\text{C}_6\text{H}_4$, forms long, colourless prisms melting at $155-156^\circ$. Benzilediparatoluidil, $\text{C}_6\text{H}_4:\text{N}:\text{CPh}:\text{CPh}:\text{N}:\text{C}_6\text{H}_4$, previously prepared by Voigt, is also formed when benzoïn-paratoluidil is heated with paratoluidine in an open vessel. *Benzoïn-paratoluidil-anilide*, $\text{C}_6\text{H}_4:\text{N}:\text{CPh}:\text{CHPh}:\text{NHPh}$, forms long, colourless needles melting at 141° . It differs from benzoïn-anil-paratoluidide, with which it is isomeric, in not being altered by repeated crystallisation. *Benzileparatoluidil-anil*, obtained by heating benzileparatoluidil with aniline in an open vessel, is in every respect identical with benzileanil-paratoluidil.

A. H.

Indoxazen Group. By O. LIST (*Ber.*, 26, 2451—2457; *Abstr.*, 1893, i, 469).—An examination of the oil obtained by nitrating deoxybenzoïn at 0° (Pictet, *Ber.*, 19, 1064) shows that it contains about

25—30 per cent. of orthonitrodeoxybenzoïn, together with benzile and benzoïn; the latter compound is obtained in large quantities when the nitration is performed at temperatures above 10° . Orthonitrodeoxybenzoïn crystallises in radiating needles, melts at $73-74^{\circ}$, gives a blue coloration with alcoholic potash, and is completely converted into α -phenylindole when treated with ammonia and zinc-dust. Its *oxime* crystallises in pale yellow needles, melts at 118° , and gives red solutions with alkalis. Nitrous acid is not eliminated from the molecule either by warming with pure sodium hydroxide, or by heating with sodium ethoxide in a sealed tube.

Paranitrodeoxybenzoïnoxime is prepared from paranitrodeoxybenzoïn, which is also obtained by nitrating deoxybenzoïn. It crystallises in yellowish-brown needles, melts at 105° , and gives a red coloration with alkalis. The author was unable to eliminate the nitro-group by treatment with alkali.

Orthonitrodeoxybenzoïn dissolved in acetic acid is easily converted into orthonitrobenzile by oxidation with chromic acid. It crystallises in yellow needles, and melts at 98° .

Orthonitrobenzileoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NOH}) \cdot \text{COPh}$, crystallises in pale yellow needles or quadratic tablets, melts at 185° with decomposition, and gives yellow solutions with alkalis. When boiled with an aqueous solution of sodium hydroxide, it yields salicylic and benzoic acids, which are formed by the decomposition of an unstable benzoylindoxazen. When boiled with sodium carbonate, salicylonitrile and benzoic acid are produced.

Orthonitrobenziledioxime is obtained by heating the monoxime with hydroxylamine hydrochloride and alcohol in a sealed tube at $120-130^{\circ}$. It crystallises in large, yellowish-white prisms, melts at 244° with decomposition, and gives red solutions with alkalis. When heated with aqueous sodium hydroxide, it yields hydroxylamine, salicylic and benzoic acids, the decomposition products of an unstable indoxazen compound of the formula $\text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{N} \geq \text{C} \cdot \text{Ph} \cdot \text{NOH}$.

Paranitrobenzile is obtained by oxidising paranitrodeoxybenzoïn with chromic acid, and is identical with the compound obtained by Hausmann by treating benzoïn with nitric acid.

The author once obtained a *second oxime of orthonitrobenzile*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CPh} \cdot \text{NOH}$, by working with a strongly alkaline solution. It melts at 265° with decomposition, and does not evolve nitrous acid when treated with sodium hydroxide.

1:4'-Dinitroanthraquinoneoxime crystallises in long, rose-red prisms, melts at 253° with a sudden decomposition, and does not lose its nitro-group when heated with concentrated sodium methoxide.

E. C. R.

Hydrocroton. By G. CIAMICIAN and P. SILBER (*Ber.*, **26**, 2635—2638).—A polemical paper, being a reply to Hesse (*Abstr.*, 1893, i, 718).

1:4-Amidoacetophthalidesulphonic acid. By A. AMMELBURG (*J. pr. Chem.*, [2], **48**, 286—292).—This acid (D.P. 66354, 1891) is prepared by sulphonating 1:4-amidoacetophthalide. It is a spar-

ingly soluble crystalline powder; a solution of it is coloured brilliantly blue by ferric chloride or chromic acid; its salts with the alkalis and alkaline earths are soluble in water. The *barium* salt crystallises with $7\text{H}_2\text{O}$; the *potassium* salt is anhydrous; the *zinc* salt crystallises with $3\frac{1}{2}\text{H}_2\text{O}$, and is freely soluble in water; the *lead* salt crystallises with $1\frac{1}{2}\text{H}_2\text{O}$, and is sparingly soluble in water.

By oxidising the acid with potassium permanganate, a little phthalic acid is produced; but when fused with potash, it yields β -hydroxyphthalic acid. The latter reaction indicates that the sulphonic group is in a β -position of the ring which does not contain the amido-groups. That this position is 2' was provisionally settled by diazotising the acid, reducing the product to the hydrazine derivative, and treating this with cupric chloride, whereby a naphthylaminesulphonic acid was produced which corresponded with Erdmann's 1:2'-acid, although the difference between the 1:2'- and the 1:3'-acids is too slight for certainty (compare Erdmann, Abstr., 1893, i, 653).

A. G. B.

Phenonaphthacridone. By M. SCHÖPFF (*Ber.*, 26, 2589—2598).—The presence of zinc chloride is not essential for the conversion of 2:3-anilidonaphthoic acid into phenonaphthacridone, as the change takes place when the former compound, or a mixture of β -hydroxy-naphthoic acid and aniline, is heated alone at 250° . A certain amount of phenonaphthacridone is obtained by heating the anilidonaphthoic acid with hydrochloric acid of 1.03 sp. gr. in a sealed tube at 180° . The most convenient method of preparing large quantities of phenonaphthacridone consists, however, in heating the anilidonaphthoic acid (250 grams), or a mixture of its components, with zinc-dust (100 grams) for 5—6 hours, in an oil-bath at 200 — 220° . The product is repeatedly boiled with dilute hydrochloric acid, and subsequently with alkali; it is crystallised from dilute alcohol, whereby the substance melting at about 240° (previously regarded as an isomeride of phenonaphthacridone) is obtained. Treatment of this substance with cold chloroform extracts phenyl- β -naphthylamine (m. p. 108 — 109°) leaving phenonaphthacridone; the supposed dihydrophenonaphthacridone obtained by distilling it with zinc-dust (Abstr., 1893, i, 476) is β -dinaphthylamine (m. p. 170.5°). Phenonaphthacridone,



has neither basic nor acidic properties, and is sparingly soluble in most solvents, the solutions exhibiting a greenish fluorescence; it is, however, readily soluble in phenol, and the solution in the latter is devoid of fluorescence; concentrated sulphuric acid dissolves it, forming a deep red solution. It crystallises from alcohol in lustrous, golden-yellow leaflets, and melts at 304 — 305° . The *ethyl* derivative, $\text{C}_{10}\text{H}_6 < \begin{smallmatrix} \text{CO} \\ \text{NEt} \end{smallmatrix} > \text{C}_6\text{H}_4$, melts at 174 — 175° ; and the *benzyl* derivative at 188 — 189° . Direct acetylation having been found impossible, the author endeavoured to prepare the acetyl derivative by heating 2:3-acetanilidonaphthoic acid, which melts at 225 — 227° ; under these

circumstances, however, phenonaphthacridone and acetic acid are formed.

Chlorophenonaphthacridine, $C_{10}H_5 < \begin{smallmatrix} \text{COI} \\ | \\ \text{N} \end{smallmatrix} > C_6H_4$, is obtained when phenonaphthacridone is heated with a mixture of phosphorus pentachloride and phosphorus oxychloride at 100—120°; it forms orange-red needles, and melts at 165°.

Phenonaphthacridine, $C_{10}H_5 < \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} > C_6H_4$, prepared by distilling phenonaphthacridone with zinc-dust, forms white needles, melts at 289°, is sparingly soluble in most solvents, but readily so in chloroform, the colourless solution having a violet fluorescence. It dissolves in glacial acetic acid, hydrochloric acid, and sulphuric acid, forming intensely red solutions. Its basic properties are feeble.

A. B. L.

α - and β -Naphthaleneindigo. By H. WICHELHAUS (*Ber.*, 26, 2547—2550).—The two isomeric forms of naphthaleneindigo can be obtained by melting 24 parts of α - or β -naphthylamine with 16 parts of chloracetic acid and 50 parts of anhydrous sodium acetate, which has been mixed with a little ordinary acetic acid. At about 180°, the mass becomes almost dry, and 50 parts of potash are then added, the temperature being raised to 290°. The product is treated with water, and the insoluble residue washed with hot, dilute hydrochloric acid, and, if necessary, extracted with ether. The crude material thus obtained is then purified by reduction, re-oxidation, and recrystallisation from aniline. α -Naphthaleneindigo crystallises from aniline in violet-black needles, whilst the β -compound separates from the same solvent in bluish, indistinct crystals. In the form of powder both isomerides show a distinct cupreous lustre when rubbed. They both sublime in needles with a cupreous lustre, the β -compound with less readiness than the α -derivative. The molecular weight of the α -isomeride was determined by the boiling point method, aniline being employed, and was found to be normal. The solubility of the β -compound in aniline was too small to admit of the determination being carried out. The reduction of these indigoes may be effected by means of hyposulphite or grape sugar in the presence of much free alkali, but is best done by warming with ferrous sulphate and potash. The formulæ of these compounds are probably quite analogous to that of ordinary indigo, $C_{10}H_7 < \begin{smallmatrix} \text{NH} \\ | \\ \text{CO} \end{smallmatrix} > \text{C}:\text{C} < \begin{smallmatrix} \text{NH} \\ | \\ \text{CO} \end{smallmatrix} > C_{10}H_7$ [$\text{NH}:\text{CO} = 1:2$ in the case of the α -compound, $= 2:1$ in that of the β -compound], but this point has not yet been definitely settled.

The characteristic colorations of ordinary indigo, and α - and β -naphthaleneindigo, are summarised in the following table.

	Ordinary indigo.	α -Naphthalene-indigo.	β -Naphthalene-indigo.
Reduction product in solution	yellow	orange	red.
Vapour	red	violet	blue.
Solution in aniline, chloroform, benzene, acetic acid, &c.	red; violet to blue	blue	bluish-green to green.
Sulphonic acid in aqueous solution	blue	blue on boiling; bluish-green in the cold	bluish-green.
Sulphonic acid on wool and silk	blue	blue to green	green.
Cotton dyed in vat	blue	blue to green	green.

The sulphonic acids are being further investigated.

A. H.

Colour of Acenaphthylene. By C. GRAEBE (*Ber.*, 26, 2354—2355).—The author is unable to obtain acenaphthylene other than coloured, and so regards it, like dibiphenylene-ethane (*Abstr.*, 1893, i, 38), as, in fact, a coloured hydrocarbon. The colour of these two substances, $\begin{array}{c} \text{CH} \\ | \\ \text{CH} \end{array} > \text{C}_{10}\text{H}_8$ and $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} > \text{C}=\text{C} < \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array}$, appears to be conditioned by the presence of the group $>\text{C}=\text{C}<$, but also by the nature of the other groups united with it (compare Armstrong, *Proc.*, 1892, 192). C. F. B.

Terpenes and Ethereal Oils. By O. WALLACH (*Annalen*, 277, 105—154).—Those terpene and terpinene compounds which are derivatives of paracymene may be distinguished by the position of the double bonds, numbering the carbon atoms in the direction of the hands of a watch from that which carries the methyl group.

Of the three theoretically possible α -keto-dihydroparacymenes, only one, the $\Delta^3,5$ modification, contains an asymmetrical carbon atom; inasmuch, therefore, as the only known representative of this series, ordinary carvone, exists in optically active modifications, it must have this constitution. The existence of four α - and four β -ketotetrahydroparacymenes is indicated by theory, and each in optically active forms, so that at least 24 modifications are rendered possible. An even greater number of hydroxy-derivatives (dihydrocarveols) is indicated, as in this case the hydroxyl group may be attached to the carbon atom carrying the alkyl groups; this is probably so in terpineol. Only two ketohexahydroparacymenes are conceivable; v. Baeyer has synthesised the α -keto-derivative (*Abstr.*, 1893, i, 359), and the β -keto-derivative is menthone. Four hydroxyhexahydrocymenes are theoretically possible, menthol being 3-hydroxyhexahydrocymene. The geometrical isomerides belonging to the last-mentioned class exhibit great differences in their physical properties, which remark also applies to the amido-derivatives (menthylamines; *Abstr.*, 1893, i, 724).

When the supposed trihydroxyterpene, $C_{10}H_{20}O_3$, obtained by oxidising terpineol (Abstr., 1893, i, 596), is heated with dilute sulphuric acid, it yields cymene, and a compound $C_{10}H_{14}O$ (see below). As terpineol appears to be a tertiary alcohol, the hydroxyl groups occupying, probably, the positions 1 or 4, the constitution of the above-mentioned oxidation product may be 1 : 2 : 4- or 1 : 3 : 4-trihydroxyhexahydrocymene.

When *terpineol dibromide* is digested on the water bath with an excess of moist silver oxide or lead oxide, pinol hydrate, $C_{10}H_{18}O_2$ (m. p. 131°) is obtained. The latter yields pinol when treated with dilute acids. Pinol (sobrerol) is also obtained in good yield when the terpineol bromide is treated with alcoholic potash. The compound $C_{10}H_{16}O$, obtained by oxidising the supposed trihydroxyterpene with chromic acid, is converted into terpenylic acid, $C_8H_{12}O_4$, when heated on the water bath with alkaline permanganate. When either of the compounds $C_{10}H_{20}O_3$, $C_{10}H_{16}O_3$, $C_{10}H_{18}O_3$ (pinolglycol), or terpenylic acid is treated in alkaline solution with bromine, carbon tetrabromide is formed.

Terpineol nitrosochloride, $C_{10}H_{18}O \cdot NOCl$, is obtained by adding ethylic nitrite to a solution of terpineol in glacial acetic acid, cooled in a freezing mixture, and subsequently dropping in hydrochloric acid; it crystallises from methylic alcohol in needles. The *piperidine*, $NO \cdot C_{10}H_{17}(OH) \cdot C_5NH_{10}$, melts at $159-160^\circ$, the *anilide* at $155-156^\circ$.

The compound $C_{10}H_{16}O$, obtained by heating the supposed trihydroxyterpene with dilute sulphuric acid, boils at $231-233^\circ$, has a sp. gr. at $20^\circ = 0.929$, and a specific refractive power $[n]_D = 1.48197$. It behaves as a ketone, in that when treated with an excess of hydroxylamine hydrochloride, it forms an oxime, $C_{10}H_{16}NOH$, melting at $91-92^\circ$, together with a compound, $C_{10}H_{20}N_2O_3$, melting at 162° ; but its molecular refractive power favours the view that it is a hydroxydihydrocymene (carveol): as such, the hydroxyl group is probably in the position 2. When the last-mentioned compound is reduced with sodium and alcohol, 2-hydroxyhexahydrocymene (tetrahydrocarveol), $C_{10}H_{18}OH$, is obtained; it boils at $218-220^\circ$, has a sp. gr. at $22^\circ = 0.904$, and a specific refractive power $[n]_D = 1.4636$. It combines with carbanil, forming an *urethane* melting at $74-75^\circ$, and, when heated at 200° with potassium hydrogen sulphite and, after the addition of alkali, distilled with steam, a hydrocarbon, $C_{10}H_{16}$ (b. p. $175-176^\circ$), passes over. When the tetrahydrocarveol is oxidised with chromic acid, a *ketone* (*tetrahydrocarvone*), $C_{10}H_{16}O$, boiling at 221° , is obtained; it has a sp. gr. at $20^\circ = 0.904$, and a specific refractive power $[n]_D = 1.45539$, and is optically inactive. On treating the ketone with nascent hydrogen, the tetrahydrocarveol is regenerated. The *oxime*, $C_{10}H_{16}NOH$, melts at 105° , and, when dissolved in dry chloroform and treated with phosphorus pentachloride, it is converted into an isomeric compound melting at $51-52^\circ$; the latter, when heated above its melting point, is converted into a third isomeride melting at 104° . When the oxime melting at 105° is reduced with sodium and alcohol, it yields *i*-amido-2-hexahydrocymene, $C_{10}H_{17}NH_2$; this boils at $211-212^\circ$, and closely resembles the menthylamines. The *hydrochloride* melts at $221-222^\circ$; the *formyl* derivative, $C_{10}H_{15}NH \cdot COH$,

obtained by distilling the *formate*, melts at 61—62°; the *acetyl* derivative melts at 124—125°; the *phenylthiocarbamide* derivative, $C_{10}H_{15}\cdot NH\cdot CS\cdot NHPh$, melts at 117°; and the *carbamide* derivative, $C_{10}H_{15}\cdot NH\cdot CO\cdot NH_2$, melts at 193—194°.

The compound $C_{10}H_{15}\cdot OH$ (see above) must be a secondary alcohol, as it was obtained by the reduction of a ketone, and the hydroxyl group must accordingly occupy positions 2 or 3. In the latter case, it would be *i*-menthol; although the latter compound is unknown, the new alcohol has not a peppermint-like odour, but one recalling that of terpineol, and its boiling point is also considerably higher than that of menthol. The tetrahydrocarveol and its derivatives described by v. Baeyer appear to differ from the author's compounds. Despite these differences, however, the author believes that the compounds described in this paper belong to the carvacrol, and not to the thymol, series. If this be so, the constitution of the above-mentioned trihydroxyhexahydrocymene will be $[(OH)_3 = 1:2:4]$, and that of terpineol 4-hydroxy- Δ^1 -tetrahydrocymene.

When pinylamine nitrate (Abstr., 1892, 997) is heated with a solution of sodium nitrite, a secondary alcohol, $C_{10}H_{15}\cdot OH$, is obtained; it has a sp. gr. at 22° = 0.978, a specific refractive power $[n]_D = 1.49787$, has a turpentine-like odour, and boils at 215—218°. On oxidation with chromic acid, it yields a *ketone* which furnishes an *oxime* melting at 98°.

Dihydrocarveol (Abstr., 1893, i, 595) appears to be converted into a trihydroxyhexahydrocymene on oxidation with permanganate; the product is not, however, crystalline, and when warmed with dilute sulphuric acid, yields an oily *oxide*, $C_{10}H_{16}O$, which boils at 196—199°, and has a pleasant, peppermint-like odour; its sp. gr. at 20° is 0.962, and its specific refractive power $[n]_D = 1.484$; it is unsaturated, and appears to react neither with hydroxylamine nor acid chlorides.

A. R. L.

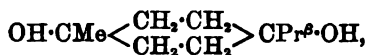
Orientation in the Terpene Series. By A. BAEYER (*Ber.*, 26, 2558—2565; compare Abstr., 1893, i, 359, 722).—Crystallised terpineol has, according to Wallach (preceding abstract), the formula

$CMe\langle\begin{smallmatrix} CH\cdot CH_2 \\ CH_2\cdot CH_2 \end{smallmatrix}\rangle CPr^s\cdot OH$. This position of the hydroxyl group is proved to be correct by the conversion of terpineol into a dihydro-compound which is identical with the tertiary menthol of the formula $CHMe\langle\begin{smallmatrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{smallmatrix}\rangle CPr^s\cdot OH$, previously described by the author.

The *methyl ether* of crystallised terpineol, obtained by the action of methylic iodide on the potassium compound, is a mobile liquid which smells like cymene, boils at 212° (corr.), and is immediately oxidised by permanganate. This substance combines with hydriodic acid to form a hydriodide, which, on reduction in ethereal solution with acetic acid and zinc, yields the methyl ether of the tertiary menthol already mentioned. This compound resembles the terpineol methyl ether, but boils at 210°, and is not acted on by permanganate.

Crude terpineol contains an isomeric substance in which the hydroxyl group occupies a different position, since the menthene obtained from the bromide prepared from the crude material is not identical

with that obtained from the crystallised portion. Terpin itself, from which terpineol is prepared, has the formula



the behaviour of the dibromide towards reducing agents showing that the hydroxyl groups are combined with carbon atoms which are not adjacent. Hence it is probable that the second constituent of crude terpineol has the formula $\text{OH} \cdot \text{CMe} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CPr}^2$. Terpin diiodide, which might be formed in small quantity by the action of hydriodic acid on terpineol methyl ether, yields, on reduction and hydrolysis of the product, a mixture of menthols which can be separated from menthyl methyl ether by treatment with potassium.

A. H.

Oximes of Cycloïd Ketones. By O. WALLACH (*Annalen*, **277**, 154—161).—When *l*-menthoneoxime (m. p. 59°) is dissolved in chloroform, and phosphorus pentachloride dropped into the solution, an isomeric *oxime* melting at 119—120°, and boiling at 295°, is obtained; its specific rotatory power in alcoholic solution is $[\alpha]_D = -52.25^\circ$ at 21°. The *hydrochloride* melts at 91—93°. Menthoneoxime, when warmed with phosphoric anhydride, is converted into a *nitrile*, $\text{C}_9\text{H}_{17}\text{CN}$, which is an oil having an intense lemon-like odour; its sp. gr. is 0.8655 at 21°, its specific refractive power $[n]_D = 1.45609$, and it boils at 220—222°. It is an unsaturated compound, yields an acid forming a sparingly soluble silver salt when boiled with alcoholic potash; and on reduction in alcoholic solution with sodium, an *amido*-compound, boiling at 210—215°, is obtained. The isomeric oxime (m. p. 105°; this vol., i, 44) can also be converted into a nitrile.

Thujonoxime melts at 54—55°, and when treated as above with phosphorus pentachloride, is converted into an *isomeride* melting at 90°; it likewise yields a *nitrile* when warmed with phosphoric anhydride.

Pulegonoxime melts at 118—119°, and the ketone regenerated from it by treatment with dilute sulphuric acid boils at 220—225°, has a sp. gr. 0.933, and a specific refractive power $[n]_D = 1.47974$ at 21°. When the oxime is reduced in alcoholic solution with sodium, a *base* is obtained which is perhaps identical with *l*-menthylamine.

A. R. L.

Formation of Trimethylsuccinic acid from Camphoric acid. By W. KOENIGS (*Ber.*, **26**, 2337—2340).—Camphoric acid was oxidised by dissolving it in very dilute aqueous soda, and allowing the solution to drop into a boiling solution of chromic and sulphuric acids. The products were carbonic anhydride and camphoronic acid, together with small quantities of an acid which melts with decomposition at 220—222°, of acetic acid, and of the trimethylsuccinic acid synthesised by Bischoff (*Abstr.*, 1891, 828). The anhydride of this last acid is volatile with steam.

When camphoroxime is oxidised by heating with rather dilute nitric acid, the products are camphoric acid, a nitrogenous substance melting at 215—218°, and Thiel's isocamphoronic acid (*Abstr.*, 1893, i, 423).

C. F. B.

Sulphocamphylic acid. By W. KOENIGS and J. HOERLIN (*Ber.*, 26, 2044—2050; compare *Abstr.*, 1893, i, 363).—Sulphocamphylic acid is readily oxidised by hot nitric acid (sp. gr. 1.25) with production of oxalic, dimethylmalonic, and sulphisopropylsuccinic acids. The two former acids are extracted by ether, and the latter is isolated by precipitating its lead salt with hydrogen sulphide. *Sulphisopropylsuccinic acid*, $C_7H_{13}SO_7 \cdot H_2O$, forms large, lustrous, tabular, colourless crystals melting at 167° with decomposition; it is readily soluble in water or alcohol, but only sparingly in ethylic acetate, chloroform, or benzene. It is a tribasic acid yielding easily soluble salts; the barium salt forms an amorphous, vitreous mass containing water, which is lost at 190 — 200° . The acid yields terebic acid, sulphurous anhydride, and water at 160 — 170° ; a small quantity of an easily soluble acid, which melts at 137 — 138° and contains no sulphur, also distils.

From the formation of dimethylmalonic acid during the oxidation of sulphocamphylic acid, Koenigs infers that camphor must contain the group $CMe_2 < \begin{smallmatrix} C \\ C \end{smallmatrix}$.

W. J. P.

Xanthorrhoea Resins. By M. BAMBERGER (*Monatsh.*, 14, 333—343).—Yellow Xanthorrhoea resin (*X. hastilis*, Sm.) was extracted with boiling 95 per cent. alcohol, the residue repeatedly boiled with water, and finally dissolved in dilute potash and acidified with dilute sulphuric acid. The crystalline material obtained from these various extracts by means of ether was then treated with chloroform, in which it partially dissolved. The portion insoluble in chloroform, on purification, proved to be paracoumaric acid, $C_9H_8O_3 + H_2O$, about 10 per cent. of the weight of the resin being obtained. The portion of the extract which was soluble in chloroform contained parahydroxybenzaldehyde, benzoic acid, and cinnamic acid. A small quantity of a substance, which was probably vanillin, was also isolated, as well as a small quantity of a white neutral substance, the nature of which was not further examined. Red Xanthorrhoea resin (*X. australis*), when treated in the same manner, yielded about 2 per cent. of paracoumaric acid, together with parahydroxybenzaldehyde and a substance resembling vanillin. Cinnamic and benzoic acids were not detected in this resin.

A. H.

Iridin, the Glucoside of Violet Roots. By G. DE LAIRE and F. TIEMANN (*Ber.*, 26, 2010—2044).—The dried roots of the violet (*Iris florentina*), on extraction with alcohol, yield a glucoside *iridin*, $C_{24}H_{38}O_{13}$; it forms slender, white needles, melts at 208° , and turns yellow in the air. Iridin undergoes hydrolysis when heated with dilute sulphuric acid at 80 — 100° , yielding *d*-glucose and *irigenin*, $C_{18}H_{26}O_8$. This substance crystallises in rhombohedra, melting at 186° . *Dibenzoylirigenin*, $C_{18}H_{14}O_8 \cdot Bz_2$, is a white, crystalline powder melting at 123 — 126° , whilst *diacetylirigenin* is a white, crystalline powder melting at 122° ; the latter forms a compound with chloroform, which is obtained in beautiful white leaflets melting at 82° . *Acetylirigenin*, $C_{18}H_{18}O_8 \cdot Ac$, is prepared by warming

the diacetyl derivative with soda, and crystallises in white needles melting at 169°.

On heating irigenin with concentrated potash, in absence of air, formic acid, iridic acid, and iretol are obtained in molecular proportion.

Iridic acid, $\text{OMe} \cdot \text{C} \begin{smallmatrix} \text{C(OMe):CH} \\ \text{-(OH)-CH} \end{smallmatrix} > \text{C} \cdot \text{CH}_2 \cdot \text{COOH}$, forms colourless prisms melting at 118°, and when heated above its melting point evolves carbonic anhydride and yields iridol. It is a strong monobasic acid, giving a well-crystallised *barium* salt, $\text{Ba}(\text{C}_{10}\text{H}_{11}\text{O}_5)_2 \cdot 5\text{H}_2\text{O}$; the *calcium* salt and those of the alkali metals are very hygroscopic. The *methyl* salt is a viscid oil boiling above 360°, whilst the *ethyl* salt is a yellow oil which decomposes on distillation under ordinary pressure. *Benzoyliridic acid*, $\text{C}_{10}\text{H}_{11}\text{O}_5\text{Bz}$, melts at 131°, and the corresponding *acetyl* derivative at 125°.

Methyliridic acid, $\text{C}_6\text{H}_5(\text{OMe})_2\text{CH}_2\text{COOH}$, forms white leaflets melting at 120°; its *silver* salt separates from alcohol in beautiful white needles.

Iridol, $\text{OMe} \cdot \text{C} \begin{smallmatrix} \text{C(OH):CH} \\ \text{C(OMe)-CH} \end{smallmatrix} > \text{CMe}$, distils on heating iridic acid at 239°; it forms large, white needles melting at 57°. The *benzoyl* derivative forms white leaflets melting at 68°.

Methyliridol, $\text{C}_6\text{H}_5\text{Me}(\text{OMe})_2$, is a colourless oil boiling at 236—237°, and on oxidation with dilute permanganate gives 3:4:5-trimethylgallic acid; it is, therefore, the trimethyl derivative of homopyrogallol. Further, on treating iridol with chloroform and caustic alkali, two isomeric aldehydes are obtained; iridol, therefore, being a dimethylhomopyrogallol, can only have the constitution assigned to it above. Iridol is isomeric with a dimethylhomopyrogallol isolated from wood-tar by Hofmann (Abstr., 1880, 248), which has the constitution $\text{Me} : \text{OH} = 1 : 4$, and may be oxidised to eupitonic acid; as would be expected from the constitution assigned to it, iridol does not yield this acid or an isomeric one under similar conditions. Both iridol and Hofmann's phenol give the same trimethylhomopyrogallol on methylation, and the same trimethylgallic acid on eliminating the methyl group from the nucleus.

Dibromomethyliridic acid, $\text{C}_6\text{Br}_2(\text{OMe})_2\text{CH}_2\text{COOH}$, is obtained by direct bromination, and forms hard crystals melting at 152°; it is very soluble in alcohol or ether. On oxidation with nitric acid, it yields *dibromotrimethylgallic acid*, which crystallises in long, brilliant needles melting at 143°. On oxidising methyliridic acid with permanganate, trimethylgallic acid is ultimately obtained, but by careful operation an α -ketonic acid of the composition $\text{C}_6\text{H}_2(\text{OMe})_2\text{CO} \cdot \text{COOH}$ may be isolated as an intermediate product. The constitutional formulæ assigned above to iridic acid and its methyl derivative are thus determined.

Iretol, $\text{C}_6\text{H}_2(\text{OH})_3\text{OMe}$ [= 2:4:6:1], is obtained by adding excess of sulphuric acid to the product obtained by heating irigenin with caustic alkali, neutralising with potassium carbonate, and repeatedly extracting with ether. On evaporating the ethereal solution, iretol remains, and is ultimately obtained in white needles melting at

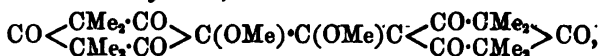
186°; it is soluble in water, alcohol, ether, and ethylic acetate, and has the normal molecular weight in acetic acid solution. Its *tribenzoyl* derivative, $C_6H_5(Obz)_3 \cdot OMe$, forms a resin. On reduction with sodium amalgam, iretol yields phloroglucinol; it therefore has the constitution stated above. *Tribenzoylphloroglucinol* crystallises in white needles melting at 172°. Iretol gives the phenolic test with ferric chloride, and combines with diazobenzene salts with formation of an insoluble red *azo*-compound; it also condenses with benzaldehyde, and with strong oxidising agents gives oxalic acid. On treatment with bromine, in absence of water, it gives hexabromacetone, and with a solution of bromine in caustic alkali, it yields bromoform. It reacts violently with phenylhydrazine or hydroxylamine; no crystalline products of these reactions could be isolated.

Sodiiodinitrosoiretol, $OMe \cdot C \begin{smallmatrix} \diagup CO \\ \diagdown C(OH) \end{smallmatrix} \begin{smallmatrix} \diagdown C(NONa) \\ \diagup C(NONa) \end{smallmatrix} > CO, H_2O$, separates as small, red crystals on treating an aqueous solution of iretol with sodium nitrite and acetic acid; it dissolves in hot water, alkalis, or acids, giving a deep red solution. On heating at 106°, it loses $2H_2O$, leaving an anhydride of the constitution $\begin{smallmatrix} CO \cdot C(OMe) : C - O \\ C(NONa) \cdot CO - C \equiv N \end{smallmatrix}$, and explodes at a higher temperature.

1:2:3:5-*Tetrahydroxybenzene* is prepared by heating iretol at 130–150° in sealed tubes with dilute hydrochloric acid; it is ultimately obtained as a syrup which slowly solidifies to an amorphous, glassy mass.

Sodiotetramethyliretol, $OMe \cdot C \begin{smallmatrix} \diagup C(ONa) \cdot CMe_2 \\ \diagdown CO \end{smallmatrix} \begin{smallmatrix} \diagdown CMe_2 \\ \diagup CMe_2 \end{smallmatrix} > CO, 3H_2O$, is obtained by heating iretol with sodium methoxide, methylic iodide, and methylic alcohol; it is precipitated by ether from its alcoholic solution in long, white needles which lose $3H_2O$ in a vacuum or at 100°. On treatment with dilute sulphuric acid, it yields *tetramethyliretol*, which forms lustrous, transparent, colourless needles containing $1H_2O$, and melting at 97°. The anhydrous substance melts at 104°; its *benzoyl* derivative forms white leaflets melting at 84°. Tetramethyliretol yields formic, isobutyric, and dimethylmalonic acids when fused with potash; its constitution is thus determined. On reducing its sodio-derivative with sodium amalgam in aqueous solution, *dihydrotetramethyliretol*, $OMe \cdot CH \begin{smallmatrix} \diagup CH(OH) \cdot CMe_2 \\ \diagdown CO \end{smallmatrix} \begin{smallmatrix} \diagdown CMe_2 \\ \diagup CMe_2 \end{smallmatrix} > CO, H_2O$, is obtained as its sodio-derivative, which forms a crystalline meal. On acidifying and extracting with ether, the phenol is set free and crystallises from water in transparent rhombs melting at 107°; it loses $1H_2O$ in a vacuum, yielding the anhydrous substance, which melts at 139° and sublimes at ordinary temperatures. It is very soluble in water, alcohol, ether, or chloroform, and is readily acted on by bromine water or permanganate.

Dehydroditetramethyliretol,



separates on warming sodiotetramethyliretol with ferric chloride

solution; it forms slender, white needles melting at 133° , is readily soluble in alcohol, ether, benzene, or chloroform, but insoluble in water, and is not at once attacked by bromine or permanganate in acetic acid solution. It has the normal molecular weight in boiling alcohol.

Pentamethyliretol, $\text{OMe} \cdot \text{CMe} < \begin{smallmatrix} \text{CO} \cdot \text{CMe}_2 \\ \text{CO} \cdot \text{CMe}_2 \end{smallmatrix} > \text{CO}$, is formed on heating sodiotetramethyliretol with methylic iodide and methylic alcohol at 100° ; it crystallises in long needles, melts at 62° , boils at 240° , and is volatile in a current of steam.

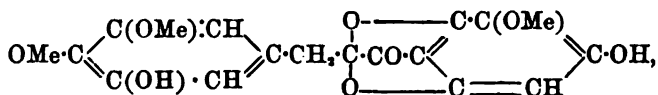
Methyliretol, $\text{C}_8\text{H}_8(\text{OMe})_2(\text{OH})_2$ [$(\text{OMe})_2 : (\text{OH})_2 = 1 : 4 : 2 : 6$ or $1 : 2 : 4 : 6$], is prepared by saturating a solution of iretol in methylic alcohol with hydrogen chloride; it is ultimately obtained in white leaflets melting at 87° .

Tetremethyliretol is precipitated by light petroleum from its chloroform solution in white prisms melting at $168-169^{\circ}$.

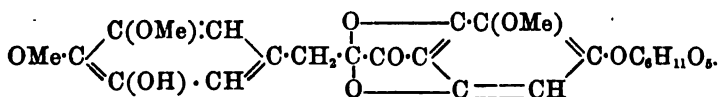
A *tripotassio*-derivative of the composition $\text{C}_{24}\text{H}_{18}\text{K}_3\text{O}_{14}$ is obtained by acting on an alcoholic solution of iridin with excess of potassium ethoxide; if less of the latter reagent is used, a *dipotassio*-derivative, $\text{C}_{24}\text{H}_{18}\text{K}_2\text{O}_{11}$, is formed. The corresponding *disodio*- and *trisodio*-compounds were also prepared; these substances form scarcely crystalline, very hygroscopic, white powders. The first product of hydrolysis of iridin therefore has the formula $\text{C}_{18}\text{H}_{14}\text{O}_8(\text{OH})_2 \cdot \text{OC}_6\text{H}_{11}\text{O}_6$, and consequently the hydrolysis of irigenin gives primarily an *α -diketone* containing four hydroxyl groups; this, on treatment with potassium cyanide in alkaline solution, gives an aldehyde and an acid, just as does benzene (Jourdan, *Ber.*, **24**, 658). On warming irigenin with dilute potash and acidifying, a precipitate is obtained which is dissolved in alcohol; on evaporating, unaltered irigenin separates, and the mother liquor, containing the products of hydrolysis, is treated with soda and potassium cyanide. After acidification, the solution is extracted with ether and a syrupy *aldehyde* is isolated from the ethereal solution by means of its compound with sodium hydrogen sulphite. The same aldehyde is obtained by treating iretol with potash, alcohol, and chloroform at the ordinary temperature; when heated with caustic alkali at 100° , it gives formic acid and iretol. These same products, together with iridinic acid, are obtained on heating irigenin with alkali. The first product of the hydrolysis of irigenin should consequently have the constitution



Irigenin can then only be considered as having the constitution



and iridin must be represented as



The qualitative solubilities of the substances are given in detail in the original. W. J. P.

Paracotoïn. By G. CIAMICIAN and P. SILBER (*Ber.*, **26**, 2340—2348).—Paracotoïn, from paracoto bark, was found by analysis and molecular weight determination to have the composition $C_{12}H_8O_4$ (probably $CH_2 \cdot O_2 \cdot C_6H_5 \cdot C_6H_5 \cdot O$), and not $C_{12}H_{12}O_6$, as is stated by Jobst and Hesse (*Abstr.*, 1880, 326); it crystallises in yellow plates melting at 151—152°. With concentrated nitric acid, it yields *dinitroparacotoïn*, $C_{12}H_6(NO_2)_2O_4$, forming yellow needles melting at 195°. With bromine in chloroform solution, it yields an unstable additive compound; this is converted by treatment with sulphurous anhydride into *bromoparacotoïn*, $C_{12}H_7BrO_4$, a substance which forms thick crystals with adamantine lustre, and melts at 200—201°. With phenylhydrazine, it does not react in acetic acid solution, but, if no third substance is present, a compound, $C_{24}H_{22}N_4O_8$, is formed, which crystallises in nodular aggregates of needles, and melts at 200—201°. With aniline (2 mols.), it forms an additive compound, $C_{24}H_{22}N_4O_8$, crystallising in nodular aggregates, and melting at 162°. Fusion with solid potash converts paracotoïn into piperonylic acid, acetopiperone, protocatechuic, formic, and another fatty (? butyric) acid. When treated with methyl alcoholic potash and methylic iodide, paracotoïn yields *dimethylparacotoïn*, $C_{12}H_8Me_2O_4$; this forms lustrous, yellow crystals, melts at 141°, and, with bromine, yields an unstable additive compound, from which the original substance is readily regenerated. Dimethylparacotoïn contains no methoxyl, for it does not yield methylic iodide when heated with hydriodic acid, and is converted by aqueous potash into the homoacetopiperone (melting at 38°) of Angeli (*Abstr.*, 1892, 1199); the authors think this last substance is more probably propiopiperone, $CH_2 \cdot O_2 \cdot C_6H_5 \cdot CO \cdot CH_2Me$. C. F. B.

Santonin. By J. KLEIN (*Ber.*, 26, 2506—2508).—By the distillation of santonin, a compound is obtained which is soluble in alkali, and crystallises from dilute alcohol in plates; it melts at 97—98° and has the formula $(C_{15}H_{13}O)_2$. The yield is small. Oxsantogenenic acid, in a similar manner, yields a compound $C_{15}H_{11}O$, which crystallises in needles, melts at 111—112°, and appears to be identical with Cannizzaro's hydrodimethylnaphthol. On heating oxsantogenenic acid at about 360°, a white powder is formed, which dissolves in chloroform, and is precipitated by alcohol; it has the same composition as oxsantogenenic anhydride, $(C_{15}H_{11}O_2)_2O$. The production of this compound is incompatible with Cannizzaro's explanation of the decomposition of santogenenic acid, since this acid has the formula $C_{15}H_{12}O_3$, and is identical with oxsantogenenic acid. α -Santogendilactone, $(C_{15}H_{11}O_2)_2O$, on distillation, yields a hydrocarbon $(C_{14}H_{10})_2$, which crystallises from ether-alcohol in needles, and melts at 93°. The ketonic group in santonin must, therefore, be in the side chain.

(compare Abstr., 1893, i, 664); the hydroxyl of the two naphthols (see above) does not correspond with that of santonic acid or santonic acid, but is linked to that carbon atom to which, in the original substance, the side chain is attached. This is a further reason for rejecting Cannizzaro's theory. J. B. T.

Constitution of Santonic acid. By S. CANNIZZARO (*Ber.*, 26, 2311—2312; compare Andreocci, Abstr., 1893, i, 526).—By the action of potash at 220° on potassium desmotroposantonate a lactone is formed, which is isomeric with desmotroposantonin, and is, therefore, termed *isodesmotroposantonin*; it melts at 187—188°, and its rotatory power is +127.55°. These compounds have identical structural formulæ, and yield isomeric acetyl derivatives, and also two desmotroposantonous acids and two isodesmotroposantonous acids which are unstable. *Isodesmotroposantonous acid* is the optical isomeride of santonic acid; each melts at 177—179°; the rotatory power of the former is -74.30°, that of the latter +74.36°; a mixture of the two in equal molecular proportions is inactive, melts at 153°, and is identical with isosantonous acid. The *ethylic salts* of the active acids melt at 116—117°, their rotatory power is -70.37° and +70.57° respectively, and they crystallise in similar forms. On admixture, the two salts combine to form a racemic compound which melts at 125°, and is identical with ethylic isosantonate. The methylic salts closely resemble the ethylic salts, and exhibit similar relationships. J. B. T.

2-Chloroquinoline. By A. CLAUS and R. KAYSER (*J. pr. Chem.*, [2], 48, 270—285).—2-Chloroquinoline dichromate is more soluble than 4-chloroquinoline dichromate, and remains in solution after the latter has been crystallised (see next abstract). The base is liberated by an alkali, and fractionally distilled in steam; it boils at 256°, and melts at 45°; it has not heretofore been crystallised, because the dichromate had not been purified, but had only been prepared in a condition in which its melting point is 109°, that of the pure salt being 121°. The *oxalate*, which melts at 145°, is a good source of the pure base. Evidence of the orientation of this chloroquinoline accrues from its preparation by Claus and Massau from 2-nitroquinoline (Abstr., 1893, i, 670). The *platinochloride* forms lustrous, yellow needles, which become darker, and melt at 255°. The *argentonitrate* melts at 120°, and dissolves in hot alcohol and hot water. The *methiodide* crystallises in long, lustrous, yellow needles, and decomposes at 172°. The *methochloride* forms small needles, which easily become coloured reddish-yellow, and melts at 122°; its *platinochloride* melts with decomposition at 246°.

1 : 2-Nitrochloroquinoline is prepared by nitrating the chloroquinoline with a mixture of nitric and sulphuric acids; it crystallises in large, vitreous, yellow needles and prisms, melts at 138°, and sublimes in colourless needles; it dissolves easily in organic solvents and in concentrated acids. The basic properties of the 2-chloroquinoline are enfeebled by the introduction of the nitro group, so that no methiodide is obtainable. The *platinochloride* is described.

1 : 2-*Amidochloroquinoline* crystallises in colourless, or slightly yellow, vitreous needles, melts at 114° , and dissolves freely in organic solvents, but only sparingly in water. It shows the feeble, basic properties characteristic of all 1-amidoquinolines; thus, it dissolves in moderately strong hydrochloric acid, with a reddish-yellow colour, which is discharged on shaking the liquid with ether, owing to the extraction of the base by this solvent; mere dilution of the hydrochloric acid solution with water will precipitate the base. The *hydrochloride*, $C_9H_7Cl \cdot NH_2 \cdot HCl$, crystallises in needles, and melts at 221° . The *platinochloride* melts, with decomposition, at 246° . The *stannochloride* forms orange-red crystals, and melts at 173° .

1 : 2-*Dichloroquinoline*, obtained through the diazo-reaction, crystallises in colourless, lustrous needles, and melts at 85.5° . Its *platinochloride* is described.

A second nitro-derivative, apparently 4 : 2-*nitrochloroquinoline*, is obtained by neutralising the nitrating liquor from which the 1 : 2-derivative has separated; it melts at 115° .

2 : 1-*Chloroquinolinesulphonic acid*, obtained by sulphonating the chloroquinoline at 150° with 30 per cent. anhydrosulphuric acid, crystallises in soft, colourless needles, and decomposes about 350° ; it is insoluble in most organic solvents, but dissolves slightly in alcohol and considerably in hot water. The *ammonium* salt, the *potassium* salt, the *silver* salt, the *chloride* (m. p. 137°), and the *amide* (m. p. 122°) were prepared. By reduction with tin and hydrochloric acid, a tetrahydroquinoline derivative, melting at 243 — 244° , was obtained, thus confirming the orientation.

A. G. B.

4-Chloroquinoline. By A. CLAUS and K. JUNGHANS (J. pr. Chem., [2], 48, 253—266).—La Conte (Abstr., 1886, 159) prepared 2- and 4-chloroquinoline, but did not succeed in separating them completely. Freydl (Abstr., 1888, 296) described derivatives of 4-chloroquinoline as those of 2-chloroquinoline.

The two chloroquinolines are separated by conversion into dichromates, of which the 4-chloroquinoline dichromate crystallises first (compare preceding abstract). It melts with decomposition at 178° .

4-Chloroquinoline forms a stellate, crystalline mass, or separate prismatic crystals, melts at 31° , boils at 268° , and dissolves slightly in hot water and freely in organic solvents. The *platinochloride* forms lustrous, orange-yellow needles; the *argentonitrate* forms flat, colourless needles, and melts at 154° ; the *methiodide* melts with decomposition at 250° ; the *methochloride* melts with decomposition about 213° , and its *platinochloride* melts with decomposition at 238° .

1 : 4-*Nitrochloroquinoline* crystallises in colourless, vitreous, transparent prisms, melts at 184° , and dissolves easily in alcohol, ether, chloroform, and concentrated acids, but not in water. The *platinochloride* melts with decomposition at 221° .

1 : 4-*Amidochloroquinoline*, obtained from the nitro-derivative in the usual manner, crystallises in colourless, vitreous needles, melts at 69° , and sublimes; it dissolves in organic solvents, but only very slightly in water. The *hydrochloride*, $C_9H_7Cl \cdot NH_2 \cdot HCl$, forms

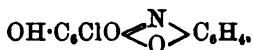
yellowish crystals, and melts at 115—116°; its solution in hydrochloric acid is intensely red. The *platinochloride* melts with decomposition at 160°. On treatment by Sandmeyer's method, the amido-derivative is converted into 1:4-dichloroquinoline (Abstr., 1893, i, 688).

During the nitration of 4-chloroquinoline, a second *nitro*-derivative is formed; it is isolated by neutralising the acid liquor, and can be crystallised in nearly colourless needles. It melts at 128°, and is more soluble in hot water than 1:4-nitrochloroquinoline; a *platinochloride* was prepared.

4: 1-*Chloroquinolinesulphonic acid* is obtained when 4-chloroquinoline is heated with 30 per cent. anhydrosulphuric acid at 150° for 10 hours. It crystallises in colourless, rhombic tables, and decomposes, without melting, at about 350°; it is insoluble in absolute alcohol and in ether, and only moderately soluble in hot water. The *potassium* salt, with $\text{1H}_2\text{O}$, the *sodium* salt, the *calcium* salt, the *barium* salt, the *ammonium* salt, the *silver* salt, the *chloride*, $\text{C}_8\text{NH}_4\text{Cl}\cdot\text{SO}_2\text{Cl}$ (m. p. 146°); the *amide*, $\text{C}_8\text{NH}_4\text{Cl}\cdot\text{SO}_2\text{NH}_2$ (m. p. 178°); and the *ethylic* salt, $\text{C}_8\text{NH}_4\text{Cl}\cdot\text{SO}_2\text{OEt}$ (m. p. 85°) are described. A. G. B.

1:4-Nitrobromoquinoline. A Correction. By A. CLAUS and G. N. VIS (*J. pr. Chem.*, [2], 48, 267—269).—In an earlier communication (Abstr., 1890, 173), the authors described 3:4-nitrobromoquinoline and 3:4-amidobromoquinoline. This orientation was deduced from the conversion of these compounds into a dibromoquinoline, which was found to melt at 124°, and was, therefore, supposed to be 3:4-dibromoquinoline, inasmuch as 1:4-dibromoquinoline was known to melt at 127—128°. They now find that they were in error when ascribing the melting point 124° to this dibromoquinoline; it is now found to be 127—128°, and, consequently, the proper orientation of the nitro- and amido-bromoquinoline should be 1:4, not 3:4. A. G. B.

Oxazine Derivatives from Orthamidophenol and Hydroxyquinones. By F. KEHRMANN and J. MESSINGER (*Ber.*, 26, 2375—2376).—Derivatives of phenoxazine may be prepared by the condensation of orthamidophenol with many hydroxyquinones. Monochloroparadihydroxyquinone, for example, yields



The product, which the authors term *chlorhydroxyphenoxazone*, crystallises from alcohol or acetic acid in yellowish-brown needles, and dissolves in alkalis and alkaline carbonates. It melts at 235° with decomposition. Acetic anhydride converts it into an *acetyl* derivative which crystallises in brownish-red needles with a green lustre, and melts at about 200° with decomposition.

The authors propose to extend the reaction described in this preliminary notice to a number of hydroxyquinones and monalkylorthamidophenols. A. H.

Action of Picrylic Chloride on Monalkylorthodiamines. By F. KEHRMANN and J. MESSINGER (*Ber.*, 26, 2372—2375).—Picrylic chloride acts on the monalkyl derivatives of the orthodiamines in the same way as on orthamidophenol (Turpin, *Trans.*, 1891, 714),



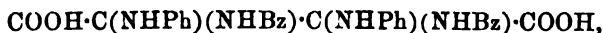
The substituted picrylorthophenylenediamines thus produced can readily be isolated, and are converted by boiling with alcohol into the corresponding dinitrodihydrophenazines, nitrous acid being eliminated.

n-Methyldinitrodihydrophenazine, $\text{C}_6\text{H}_3(\text{NO}_2)_2\langle\begin{smallmatrix} \text{N}\cdot\text{Me} \\ \text{NH} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$, forms dark violet, flaky crystals with a cupreous lustre. It melts with decomposition at 240° , and is readily soluble in hot ethylic benzoate, but only slightly in other solvents. The cold solutions are olive-green, but become an intense reddish-violet when heated. It dissolves without change in sulphuric acid, and forms a deep blue solution in cold alcoholic potash. The solution in acetic acid decomposes on boiling, nitric oxide being evolved. *n*-Ethyldi-nitrodihydrophenazine forms small needles resembling sublimed indigo, and melts at 246° with decomposition. In solubility, it resembles the methylic derivative. *n*-Benzoyldinitrodihydrophenazine separates from boiling benzene in tablets which have a violet metallic lustre, and melts at 240° with decomposition. *n*-Phenyldinitrodihydrophenazine prepared from orthamidodiphenylamine melts at 246° .

Dinitrodihydrophenazine, $\text{C}_6\text{H}_3(\text{NO}_2)_2\langle\begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$, can be obtained with some difficulty from the product of reaction of orthophenylenediamine and picrylic chloride. A. H.

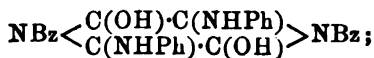
Hippuroflavin. By L. RÜGHEIMER and A. KÜSEL (*Ber.*, 26, 2319—2327).—Hippuroflavin, $\begin{array}{c} \text{CO}-\text{C}-\text{NBz} \\ | \quad | \\ \text{NBz}-\text{C}-\text{CO} \end{array}$, has been previously prepared by the action of phosphorus pentachloride on ethylic hippurate (*Ber.*, 21, 3321); an intermediate compound, $\text{CPhCl}\cdot\text{N}\cdot\text{CHCl}\cdot\text{COOEt}$, is first formed, and hydrogen chloride and ethylic chloride are then eliminated. In support of this view, the authors have obtained *ethylic hydroxyhippurate*, $\text{NHBz}\cdot\text{CH}(\text{OH})\cdot\text{COOEt}$, by treating the product formed by heating ethylic hippurate and phosphorus pentachloride at 140° , with ice; it crystallises in small, colourless needles melting at 114 — 115° . Hippuroflavin resembles quinone in some of its reactions, and yields unstable additive products with phenols, and stable compounds with aniline bases. With ordinary phenol, the compound $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_4\cdot 2\text{C}_6\text{H}_5\text{OH}$ is formed, and crystallises in colourless needles; it is resolved into its constituents on heating or by boiling with dilute alcohol. *Dianilidohippuroflavin*, $\text{NBz}\langle\begin{array}{c} \text{CO}\cdot\text{C}(\text{NHPh}) \\ \text{C}(\text{NHPh})\cdot\text{CO} \end{array}\rangle\text{NBz}$, is formed by boiling hippuroflavin with aniline in excess; it is sparingly soluble, crystallises from benzene or glacial acetic acid in pale yellow needles, and melts at $234\cdot 5$ — $235\cdot 5^\circ$. By the action of

alcoholic potash, it is decomposed with formation of ammonia; with aqueous alkalis, it undergoes hydrolysis, two acids being obtained. The one is monobasic, has the formula $\text{CO} \cdot \text{C}(\text{NHPh}) \cdot \text{NHBz}$ and $\text{NBz} \cdot \text{C}(\text{NHPh}) \cdot \text{COOH}$, and crystallises from alcohol in small needles which melt at $226-227^\circ$ with decomposition. The second acid, which is bibasic, appears to be *dibenzamidodianilidosuccinic acid*,



and crystallises in broad, stellate needles melting at $221-222^\circ$.

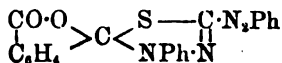
Anilidohippuroflavin, $\text{CO} \cdot \text{CH} \text{---} \text{NBz}$
 $\text{NBz} \cdot \text{C}(\text{NHPh}) \cdot \text{CO}$, is obtained together with the dianilide; it crystallises in small, yellow needles, and melts at $189-192^\circ$. Toluidine, xyldine, and methylaniline also react with hippuroflavin, giving compounds corresponding with the monoanilide; dimethylaniline does not combine with hippuroflavin. The formation of the above anilido-compounds does not take place directly, but is preceded by that of *dihydroxydianilidohippuroflavin*,



this is a colourless substance, and melts at $258-260^\circ$. The corresponding orthotoluidine derivative crystallises from glacial acetic acid, and melts at $235-238^\circ$. Both compounds are almost insoluble in ordinary media, they are feebly basic (phenolic), dissolve in alcoholic potash, and are reprecipitated on the addition of water. On heating with alcoholic potash or nitrobenzene, hydrogen is eliminated, and the yellow anilido-derivatives are formed. It is at present uncertain whether the $\text{C}(\text{OH})\text{C}(\text{NHPh})$ groups in dihydroxydianilidohippuroflavin are doubly linked in the ortho- or para-position. J. B. T.

Action of Thionic, Phthalic, and Succinic Chlorides on Phenylhydrazine. By M. FREUND and S. WISCHEWIANSKY (*Ber.*, 26, 2494-2496).—*Thionyl-ψ-diphenylthiocarbazon*, $\text{SO} \text{---} \text{S} > \text{C} \cdot \text{N}_2\text{Ph}$,
 $\text{NPh} \cdot \text{N}$

is prepared by the action of thionic chloride on diphenylthiocarbazon in benzene solution at ordinary temperatures, and is deposited from benzene-alcohol in yellow crystals which melt at $144-145^\circ$. It is stable towards aqueous alkalis, but, on boiling with alcohol or alcoholic potash, is resolved into its components. The letter ψ is employed by the authors to indicate that the phenylhydrazine derivative reacts in its pseudo-form. By the treatment of the carbazon with alcoholic ammoniac sulphide, it is converted into *thionyl-ψ-diphenylcarbizine*, $\text{C}_6\text{H}_5\text{N}_2\text{S}_2\text{O}$, which is crystalline, melts at 162° , and is readily oxidisable. *Phthalyl-ψ-diphenylcarbazone*,



is prepared from phthalic chloride and diphenylthiocarbazon, and

crystallises from alcohol or glacial acetic acid in yellow plates melting at 182° ; the compound is resolved into its components by treatment with alcoholic potash. Succinyldiacetylphenylhydrazine is prepared from succinic chloride and acetylphenylhydrazine, and has been previously obtained by Michaelis. *Succinyldiformylphenylhydrazine*, $C_8H_7(CO \cdot NPh \cdot NH \cdot CHO)_2$, is formed from succinic chloride and formylphenylhydrazine; it is crystalline, and melts at $246-247^{\circ}$. No definite compounds could be obtained by the action of succinic chloride on diphenylsulphocarbazono or of thionyl chloride on acid derivatives of phenylhydrazine. J. B. T.

Triazole Derivatives from Amidoguanidine. By J. THIELE and K. HEIDENREICH (*Ber.*, 26, 2598-2602).—*Amidomethyltriazole*,

$NH_2 \cdot C \begin{smallmatrix} \nearrow NH \cdot N \\ \searrow N - CMe \end{smallmatrix}$, is obtained by dissolving acetamidoguanidine nitrate (*Abstr.*, 1892, 1297) in aqueous sodium carbonate, and evaporating the solution to dryness; it crystallises from boiling glacial acetic acid in stellate groups of white needles, and melts at 148° ; the silver salt is insoluble in water; the nitrate melts at 171° ; and the picrate melts at 225° with decomposition.

Azomethyltriazole, $\begin{smallmatrix} N \cdot NH \\ | \\ CMe \cdot N \end{smallmatrix} > C \cdot N : N \cdot C \begin{smallmatrix} \nearrow NH \cdot N \\ \searrow N - CMe \end{smallmatrix}$, is formed when the amido-derivative is oxidised with permanganate in presence of a large excess of alkali; it dissolves in alkalis, but is insoluble in all indifferent solvents, forms a yellow powder, and decomposes at a very high temperature without melting. The silver salt is a voluminous precipitate. When the azo-derivative is reduced with stannous chloride, *hydrazomethyltriazole* is obtained; the hydrochloride crystallises in six-sided prisms, is sparingly soluble in concentrated hydrochloric acid, insoluble in alcohol and ether, and melts at 250° with decomposition. A. R. L.

New Triazole and Triazine Derivatives. By O. WIDMANN (*Ber.*, 26, 2612-2617).—*Hydroxyphenyltriazole*, $NPh \begin{smallmatrix} \nearrow CH \cdot N \\ \searrow N = COH \end{smallmatrix}$, is

obtained by boiling phenylsemicarbazide with concentrated formic acid ($2\frac{1}{2}$ parts) in a reflux apparatus for $7\frac{1}{2}$ hours; it is almost insoluble in nearly all ordinary solvents, and melts at a very high temperature. The hydrochloride, $C_8H_7N_3O \cdot HCl + H_2O$, crystallises in fan-shaped groups of needles. When the silver salt, $C_8H_7N_3O \cdot Ag + H_2O$, is strongly heated, phenyltriazole sublimes and a residue of metallic silver remains; the same phenyltriazole is also obtained by heating the hydroxy-derivative with phosphoric sulphide; it agrees in properties with Andreocci's phenylpyrroldiazole (*Abstr.*, 1892, 636). The platinumchloride, $(C_8H_7N_3)_2 \cdot H_2PtCl_6$, if heated at 180° , becomes a paler yellow with the loss of hydrogen chloride (2 mols.), and the formation of the salt $(C_8H_7N_3)_2 \cdot PtCl_4$.

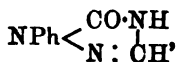
Diphenyltetrahydrotriazine, $NPh \begin{smallmatrix} \nearrow CO \cdot CH_2 \\ \searrow N = CH \end{smallmatrix} > NPh$, is obtained by boiling α -phenylamidacetylphenylhydrazide,



with anhydrous formic acid; it melts at 173—174°.

A. R. L.

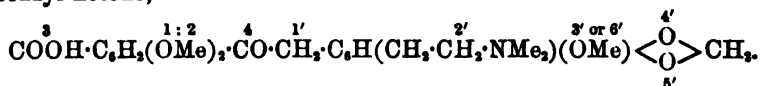
Constitution of the Triazole and Tetrazole Derivatives prepared by Andreocci and by Bladin. By O. WIDMANN (*Ber.*, 26, 2617—2621).—The hydroxyphenyltriazole described in the last abstract is isomeric with Andreocci's compound (*Reg. Univers. d. Studi Roma*, 1890—1891, 469), and must have the constitution,



assigned to it by this chemist, and not that proposed by Bladin. The formulæ of all Bladin's triazole and tetrazole derivatives require alteration. It also follows that dicyanophenylhydrazine has the constitution $\text{NPh}\cdot\text{N}:\text{C}(\text{CN})\cdot\text{NH}_2$. (Compare this vol., i, 23.)

A. R. L.

Narceïne. By M. FREUND and G. B. FRANKFORTER (*Annalen*, 277, 20—58).—The authors find that Anderson's formula for narceïne, $\text{C}_{23}\text{H}_{28}\text{NO}_8 + 2\text{H}_2\text{O}$, which is the generally received one, requires modifying to $\text{C}_{23}\text{H}_{27}\text{NO}_8 + 3\text{H}_2\text{O}$. The hydrated compound melts at about 170°, and loses $2\text{H}_2\text{O}$ readily at 100°, the third mol. being expelled with greater difficulty; the anhydrous compound melts at 140—145°, is very hygroscopic, unites with 1 mol. H_2O when exposed to the air, and then melts above 160°. The base obtained by Roser by heating narcotine methiodide with alkali, and named by him pseudo-narceïne (*Abstr.*, 1888, 1316), is identical with narceïne. Assuming that the group CH_2O_2 , in narcotine, occupies the same position as in hydrastine, narceïne may be represented as a substituted phenyl benzyl ketone,



The alkaloid thus contains no asymmetrical carbon atom; this is in accord with its optical inactivity. The above constitutional formula is fully in agreement with the behaviour of the alkali salts of the alkaloid.

The *potassium* and *sodium* salts of narceïne are obtained by heating the base at 60—70° with 33 per cent. aqueous alkali; on adding ether to their alcoholic solutions, the salts are precipitated in crystals containing 1 mol. EtOH . The *potassium* salt melts at 90°, and the *sodium* salt at 159—160°. The alkaloid is regenerated when the alkali salts are treated with acids or carbonic anhydride. Crude narceïne may be purified by means of the sodium salt. The *barium* salt melts at 182°, the *lead* salt at about 157°, and the *copper* salt decomposes at 172°.

Sodium narceïne gives with the undermentioned reagents the following compounds:— $\text{C}_{23}\text{H}_{26}\text{EtNO}_8\cdot\text{MeI}$ (m. p. 203°), with methylic iodide and ethylic alcohol; $\text{C}_{23}\text{H}_{26}\text{MeNO}_8\cdot\text{MeI}$ (m. p. 193—194°), with methylic iodide and methylic alcohol; $\text{C}_{23}\text{H}_{26}\text{EtNO}_8\cdot\text{EtI}$ (m. p. 131—132°), with ethylic iodide and ethylic alcohol; $\text{C}_{21}\text{H}_{24}\text{MeNO}_8\cdot\text{EtI}$

(m. p. 203°). with ethylic iodide and methylic alcohol; $C_{23}H_{28}EtNO_6.C_2H_5I$ (m. p. 154—155°), with allylic iodide and ethylic alcohol; $C_{23}H_{28}MeNO_6.MeI$, with methylic iodide and ether. *Methylic narceïne* (see below) is obtained by boiling the sodium salt with methylic alcohol.

Narceïne hydrochloride crystallises with $5\frac{1}{2}H_2O$ and $3H_2O$; the anhydrous salt melts at 190—192°. The *platinochloride* crystallises with $2H_2O$, melts at 190—191°, and decomposes at 195—196°; the *nitrate* decomposes at 97°; the *sulphate* loses its water of crystallisation when kept in a partial vacuum.

Methylic narceïne forms a *hydrochloride* which crystallises from water in rectangular tables, and melts at 149°; the *platinochloride* melts at 205—206°; the *hydrobromide* melts at 148°; and the *hydriodide* melts at 139°. *Ethylic narceïne hydrochloride* melts at 206—207°; the *platinochloride* melts at 194—195°; the *hydrobromide* melts at 215—216°; and the *hydriodide* melts at 212°.

A determination by Zeisel's method established the presence of three methoxy-groups in narceïne. When narceïne is boiled with a solution of hydroxylamine hydrochloride, and ammonia is added to the product, the *oxime anhydride*, $C_{23}H_{28}N_2O_7$, is precipitated; it separates from alcohol in white crystals, melts at 171—172°, and forms a *hydrochloride* melting at 206—208°. When the anhydride is treated with potash, the *oxime*, $C_{23}H_{28}N_2O_8 + H_2O$, is obtained; it decomposes at 167°. The *phenylhydrazone hydrochloride*, $C_{23}H_{31}N_3O_6.HCl$, melts at about 175°, resolidifies above this temperature, and again melts at 215—220°. This modification of higher melting point is also obtained by crystallising the lower melting compound from hot absolute alcohol.

If narceïne is heated at 100° for three hours in a sealed tube, with excess of methylic iodide, a resinous mass is formed; when it is heated with potash, trimethylamine passes over, and the potassium salt of *narceonic acid*, $C_{21}H_{20}O_6$, remains in solution; the pure acid crystallises in white, lustrous, six-sided prisms, and melts at 208—209°.

The authors failed to obtain the additive compounds of narceïne with ethylic bromide and benzylic chloride, described by Claus and Ritzefeld (Abstr., 1885, 996). By oxidising narceïne with acid and alkaline permanganate, and also with nitric acid, hemipinic acid was obtained, but the formation of Claus and Meixner's narceinic acid (Abstr., 1888, 612) was not observed.

A. R. L.

Note by Abstractor.—Besides the derivatives of narceïne described in this abstract, in most cases the corresponding derivatives of the so-called pseudonarceïne were also prepared. Although the authors conclude that the compounds from both sources are identical, it is to be noticed that the melting points recorded of the derivatives of pseudonarceïne are distinctly higher than those from narceïne.

Action of Methylic Iodide on Papaverinic acid. By F. SCHRANZHOFER (*Monatsh.*, 14, 521—535; compare Abstr., 1889, 1016).—When papaverinic acid, methylic iodide, and methylic

alcohol are heated together in sealed tubes at 100° for 18—19 hours, two products are obtained, one of which is readily soluble in acetone, whilst the other is only sparingly soluble. The latter the *methylbetaine* of *papaverinic acid*, $C_{17}H_{16}NO_7 + H_2O$, when obtained free from iodine, crystallises in yellow, transparent plates, melts with decomposition at 192 — 194° , and dissolves in sodium carbonate solution with evolution of carbonic anhydride. It is a monobasic acid, forms crystalline *silver* and *barium salts*, and a *hydrochloride*, crystallising in yellow prisms, and melting with decomposition at 182 — 184° . The *platinochloride*, $(C_{17}H_{16}NO_7)_2 \cdot H_2PtCl_6 + H_2O$, is not well characterised. That portion of the product above-mentioned which is soluble in acetone is resolved, on distillation, into two substances. Of these, one is the *methyl salt* of the *methylbetaine* of *papaverinic acid*, $C_{18}H_{17}NO_7$; it crystallises in large, white plates, melts at 122 — 124° , and becomes rose-coloured on exposure to the light. The other is an isomeride of the betaine, $C_{17}H_{16}NO_7$, described above; it crystallises in white, microscopic needles, which are anhydrous, is insoluble in ether, sparingly soluble in water, melts at 195 — 197° , and appears, from an analysis of its barium salts, to be a bibasic acid.

G. T. M.

Hydrastine. By M. FREUND and F. LUTZE (*Ber.*, 26, 2482—2490).—*Benzylhydrastine*, $C_{21}H_{23}NO_6 \cdot C_6H_5$, is prepared by warming the hydriodide (see below) with potash, and is deposited from alcohol in yellow crystals melting at 135° . The *hydrochloride*, $C_{28}H_{27}NO_6 \cdot HCl$, melts at 224° . The *hydrobromide*, $C_{28}H_{27}NO_6 \cdot HBr$, melts at 228° . The *nitrate* melts at 177° . The *hydriodide* is formed by the action of benzylic iodide on hydrastine in alcoholic solution; it crystallises from water, and melts at 177° . The *hydroxide*, $C_{21}H_{21}NO_6 \cdot C_6H_5 \cdot OH$, is obtained from the chloride by treatment with silver oxide, and is deposited in needles which contain water of crystallisation, and melt at 194° . *Benzylhydrastamide*, $C_{28}H_{29}N_2O_6$, is prepared from the hydriodide by the action of ammonia, and melts at 116° . By the action of mineral acids, or of concentrated alkalis on the amide, the imide, $C_{28}H_{25}N_2O_6$, is obtained in pale yellow crystals melting at 140° ; its *hydrochloride* melts at 156° ; the *methiodide* and *ethiodide* are crystalline, and melt at 230° and 232° respectively. *Benzylhydrastine*, $C_{28}H_{27}NO_7$, is prepared by boiling benzylhydrastine with concentrated potash, and crystallises from alcohol in colourless needles which melt at 159° . The *oxime anhydride*, $C_{28}H_{25}N_3O_6$, is formed by the action of aqueous hydroxylamine hydrochloride on the preceding compound, and crystallises from alcohol in pale yellow needles melting at 135° .

J. B. T.

Organic Chemistry.

Metallic Derivatives of Acetylene. By E. H. KEISER (*Amer. Chem. J.*, 15, 535—539; compare Abstr., 1892, 1416).—When acetylene is passed into a solution of mercuric iodide in potassium chloride to which caustic potash has been added, a compound C_2Hg is precipitated in white flakes. This substance explodes violently when heated, dissolves in hydrochloric acid with evolution of acetylene, and, when treated with an alcoholic solution of iodine, yields di-iodo-acetylene, which polymerises, after a time, to crystals that melt at 187° ; probably of hexiodobenzene.

When acetylene is passed into a saturated aqueous solution of mercuric chloride, a compound $C_2(HgCl)_2 + \frac{1}{2}H_2O$, is obtained as a granular, white precipitate. It explodes but feebly when heated, and does not dissolve in dilute hydrochloric acid. C. F. B.

Decomposition of Chloroform. By C. SCHACHT and E. BILTZ (*Pharm. J. Trans.*, 52, 1005—1006).—Chloroform is not decomposed by the action of sunlight unless oxygen is present, when, in the first stages of the decomposition, chlorine is liberated, and this, acting on the alcohol contained in the chloroform, produces hydrogen chloride, which is then found instead of free chlorine. Hence the liberation of chlorine has been disputed by some who have overlooked the presence of alcohol in the chloroform operated on. Pure chloroform begins to decompose immediately in strong daylight, but the addition of alcohol prevents or arrests the decomposition, and will, moreover, on agitation of the liquid, remove any free chlorine and also any carbon oxychloride already liberated. The authors have found that the addition of 0.25 per cent. of alcohol suffices to preserve chloroform for at least a month in average daylight; 0.5 per cent. will preserve it for a year; and 1 per cent. for many years. The amount of alcohol in a sample may be inferred from the specific gravity, which at 15° is for pure chloroform, 1.5020; with 0.25 per cent. alcohol, 1.4977; with 0.5 per cent., 1.4939; with 1 per cent., 1.4854; with 2 per cent., 1.4705. R. R.

Isocyanogen Tetrabromide (Tetrabromoformalazine). By J. THIELE (*Ber.*, 26, 2645—2647; compare Pulvermacher, this vol., i, 12).—Amidotetrazotic acid (Abstr., 1892, 1299) yields, on oxidation in alkaline solution, salts of azotetrazole, $\begin{array}{c} \text{N}-\text{N} \\ \parallel \quad \parallel \\ \text{N}-\text{NH} \end{array} > \text{C} \cdot \text{N} \cdot \text{N} \cdot \text{C} < \begin{array}{c} \text{N}-\text{N} \\ \parallel \quad \parallel \\ \text{NH} \cdot \text{N} \end{array}$.

The hydrazotetrazole obtained by reducing the latter, when treated with bromine, furnishes isocyanogen tetrabromide (tetrabromoformalazine), $\text{CBr}_3 \cdot \text{N} \cdot \text{N} \cdot \text{CBr}_3$; this crystallises from glacial acetic acid in large, lustrous prisms, is insoluble in water, melts at 42° , and is readily volatile with steam, the warm vapour attacking the

mucous membrane. When warmed with concentrated sulphuric acid, carbonic anhydride and hydrogen bromide are evolved, and water precipitates hydrazine sulphate from the solution. The tetrabromide dissolves when gently warmed with alkalis, and hydrazine is only recognised in the solution after acidification; if the alkaline solution is distilled, the last fraction contains a compound which is, perhaps, isocyanogen oxide, $\text{CO}\cdot\text{N}\cdot\text{N}\cdot\text{CO}$, or a polymeride. When an oxidisable substance is present, a strong odour recalling that of an isonitrile is recognised, which may be due to isocyanogen, $\text{C}\cdot\text{N}\cdot\text{N}\cdot\text{C}$.

A. R. L.

Action of Chlorine on Ethylic Alcohol. By M. ALTSCHUL and V. MEYER (*Ber.*, 26, 2756—2759).—The authors have examined an oily liquid which is obtained as a bye-product in the manufacture of chloral by the action of chlorine on ethylic alcohol. The oil was separated from admixed chalk and calcium chloride by distillation with steam, and, on rectification, three fractions were obtained: the first portion ($60\text{--}90^\circ$) consists largely of chloroform, which appears to be formed by the action of the steam on trichloroacetic acid. The second fraction ($90\text{--}140^\circ$) has not yet been investigated; the third ($140\text{--}168^\circ$) consists of ethylic dichloroacetate, trichloroethylic alcohol, and probably dichloroethylic alcohol. Ethylic dichloroacetate was identified by the production of ethylic iodide and dichloroacetamide; the trichloroethylic alcohol yields a metanitrobenzoate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COO}\cdot\text{C}_2\text{H}_5\cdot\text{Cl}_3$, crystallising in transparent plates; it melts at 75° , and is identical with the compound prepared from pure trichloroethylic alcohol.

J. B. T.

New Method of preparing Ethylic Ether and its Homologues. By F. KRAFFT (*Ber.*, 26, 2829—2833).—In the preparation of ether by means of sulphuric acid, the latter compound undergoes a certain amount of reduction to sulphurous acid; this being due to the alcohol. In point of stability towards alcohol, the aromatic sulphonic acids are superior to sulphuric acid. The author shows (see also this vol., i, 91) that the aromatic sulphonic acids can be employed for the continuous etherification of alcohols in the same manner as sulphuric acid. Thus in the case of ethylic alcohol and benzenesulphonic acid: $\text{PhSO}_3\cdot\text{OH} + \text{EtOH} = \text{PhSO}_3\cdot\text{OEt} + \text{H}_2\text{O}$; $\text{PhSO}_3\cdot\text{OEt} + \text{EtOH} = \text{PhSO}_3\cdot\text{OH} + \text{Et}_2\text{O}$; the alcohol is dropped on to the benzenesulphonic acid heated to about 140° . Methyl propylic ether was prepared by this method from a mixture of methylic and propylic alcohols; it was found to boil at $36\cdot6\text{--}37\cdot4^\circ$ (752 mm.), and its sp. gr. at 0° was 0.7460 (compare Henry, *Abstr.*, 1892, 27).

A. R. L.

Synthesis of Erythritol and of an Isomeride. By G. GRINER (*Compt. rend.*, 117, 553—556).—The unstable liquid obtained by the action of bromine on erythrene at a low temperature (*Abstr.*, 1893, i, 450) is the dibromide, $\text{CH}_2\cdot\text{CH}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, which, when treated with bromine, yields the tetrabromide described by Ciamician and Magnaghi. It is isomeric with the solid dibromide,



which served for the synthesis of erythritol (*loc. cit.*). When these dibromides are treated with a 1 per cent. aqueous solution of potassium permanganate in presence of alcohol at about 0°, the liquid dibromide yields a dibromhydrin melting at 135°, identical with that obtained by Champion by the action of hydrobromic acid on erythritol, and yielding a diacetin, $C_6H_4Br_2O_2Ac_2$, melting at 133–134°, whilst the solid dibromide yields a dibromhydrin melting at 83°, and a diacetin melting at 96°.

The dibromhydrins may be converted into tetracetins, but the process has the disadvantage of requiring somewhat high temperatures. It is more convenient to convert them into dioxides by the action of dry, solid potassium hydroxide at the ordinary temperature, the dioxides being afterwards converted into the corresponding tetrahydric alcohol by heating with water below 100°.

The liquid dibromide yields a dioxide which melts at 4°, and boils at 59–60°, under a pressure of 30 mm.; it is soluble in alcohol and water; sp. gr. at 16° = 1.113. When its aqueous solution is heated on a water-bath, it yields a compound $C_6H_{10}O_4$, crystallising from alcohol in small, silky tufts melting at 72°, very soluble in water, and even deliquescent; more soluble in alcohol than ordinary erythritol. This compound yields a tetracetin, $C_6H_4O_4Ac_4$, melting at 53°, and is an isomeride of ordinary erythritol.

The solid dibromide in like manner yields ordinary erythritol by conversion into a dioxide, and subsequent hydration of the latter (compare *loc. cit.*).
C. H. B.

Iodide of Starch. By G. ROUVIER (*Compt. rend.*, 117, 461).—Measured volumes of starch and iodine solutions of known strength were mixed together, and concentrated sodium chloride solution was added. After some time, the iodine in the precipitate and that remaining in solution was determined by means of thiosulphate solution. The quantity of iodine taken up by a given quantity of starch increases with the quantity of iodine solution added, until it reaches a maximum corresponding with the formula $(C_6H_{10}O_5)_{16}I_2$, beyond which no further combination takes place, even with a large excess of iodine.

With a given weight of iodine and starch, the quantity of iodine remaining uncombined increases with the volume of the liquid, provided that the proportion of iodine is not greatly in excess of that required to give a compound containing 19.6 per cent., or the maximum quantity, of iodine. If this proportion is exceeded, an increase in the total volume of the liquid does not prevent the formation of the compound $(C_6H_{10}O_5)_{16}I_2$ (compare *Abstr.*, 1892, 578, 801, and 1171, and 1893, i, 683).
C. H. B.

Chemistry of Plant Fibres: Celluloses, Oxycelluloses, and Lignocelluloses. By C. F. CROSS, E. J. BEVAN, and C. BEADLE (*Chem. News*, 68, 225–227; also *Ber.*, 26, 2520–2533).—Collating work done by them on jute fibre—the simplest type of lignification—the authors note that by chlorination this fibre yields 72 to 75 per cent. of α -cellulose, but, by treatment with dilute nitric acid, or by repeated

bromination, or by regulated oxidation with chromic acid, the yield of α -cellulose is 60—63 per cent. Moreover, the cellulose of jute fibre under hydrolysis with hydrochloric acid yields but traces of furfuraldehyde, whereas 6 per cent. of this aldehyde is obtained from it by means of a mixture of concentrated sulphuric acid and aqueous hydrochloric acid; under similar treatment, more resistant celluloses, such as cotton cellulose, yield only a few tenths per cent., unless they have been previously subjected to oxidation, then the yield of furfuraldehyde may attain 8 per cent.; it seems, therefore, that jute fibre cellulose is an oxycellulose; and, in addition, about one-sixth of the cellulose obtained by chlorination consists of β -cellulose containing two methoxyl-groups in the formula weight, $C_{15}H_{22}O_{10}$.

The non-celluloses, either in the raw fibre or in the chlorinated fibre, give over 9 per cent. of furfuraldehyde when boiled with hydrochloric acid; they also contain over 14 per cent. of methoxyl, and when rendered soluble by chlorination, yield quinone chlorides corresponding to 7—9 per cent. (on the fibre substance) of keto-R-hexene derivatives; these derivatives are assumed to contain groups of the general form $CO < \begin{smallmatrix} CH & \text{---} & CH \\ C(OH)_2 & & C(OH)_2 \end{smallmatrix} > CH_2$, condensed by union of OH groups. The remaining portion of the non-celluloses consists of the complex $C_{15}H_{16}O_8$. Jute fibre is therefore regarded as consisting of 60—65 per cent. of α -cellulose, 15—20 per cent. of β -cellulose, 7—9 per cent. of keto-R-hexene derivatives, and 18—22 per cent. of the above complex, and these substances appear to be so related chemically as to suggest a series of transitions from one extreme member to the other.

Incidentally it is noted that, according to the authors' views, the production of furfuraldehyde does not depend on the presence of a pentaglucose.

D. A. L.

Preparation of Methylamine: Constitution of Hexamethylenetetramine. By A. TEILLAT and FAYOLLAT (*Compt. rend.*, 117, 628—630).—100 grams of a 33 per cent. solution of formaldehyde is mixed with a cold aqueous solution of ammonia until there is no further development of heat, 200 grams of zinc powder is added to the mixture all at once, and then 750 grams of ordinary hydrochloric acid very gradually, the operation occupying from eight to ten hours. The product is now mixed with a large excess of sodium hydroxide, and distilled in a current of steam, the distillate being received in dilute hydrochloric acid; ammonia passes over first, and methylamine afterwards, the two hydrochlorides being separated by means of alcohol, after evaporating to dryness. The methylamine thus obtained is free from secondary and tertiary amines.

It would seem that the action of ammonia on formaldehyde yields the compound $CH_2(N:CH_2)_3$, and the latter is then reduced, yielding $CH_2(NHMe)_3$, which, by the action of water, is converted into formaldehyde and methylamine.

The authors consider that the constitution of the product of the action of ammonia on formaldehyde is more probably $CH_2(N:CH_2)_3$, than $N_4(CH_2)_6$. The first product of the reaction may be methylene-

amine, CH_3NH_2 , which reacts with a further quantity of aldehyde, $2\text{CH}_3\text{NH}_2 + \text{CH}_2\text{O} = \text{CH}_3(\text{N}:\text{CH}_2)_2 + \text{H}_2\text{O}$. It is known that, with formaldehyde, aniline yields the compound CH_3NPh , whilst monomethylaniline gives the compound $\text{CH}_3(\text{NPhMe})_2$. C. H. B.

Nitrites of Amines. By W. A. NOYES (*Amer. Chem. J.*, 15, 539—546).—The nitrites of some amines of the type CHR_2NH_2 have been prepared, and found to be stable at the ordinary temperature; they are, however, decomposed, with evolution of nitrogen, when their solutions are boiled or evaporated to dryness. The amines were in general prepared by reducing the corresponding ketoximes.

Diethylcarbinamine, $\text{CH}_3\text{Et}_2\text{NH}$, is a colourless liquid boiling at $89-91^\circ$, of sp. gr. 0.7487 at $20^\circ/4^\circ$; the *hydrochloride* crystallises in needles melting at $216-217^\circ$; the *platinochloride* in needles; and the *nitrite* in deliquescent, white needles. *Dipropylcarbinamine*, $\text{CH}_3\text{Pr}_2\text{NH}$, is a colourless liquid, boils at $139-140^\circ$, and has a sp. gr. 0.7667 at $20^\circ/4^\circ$. The *hydrochloride* crystallises in needles melting at $241-242^\circ$; the *platinochloride* in pale yellow scales; the *nitrite* is decomposed by boiling, much more rapidly in concentrated than in dilute solution. *Di-isobutylcarbinamine* is a colourless liquid, boils at $166-167^\circ$, and has the sp. gr. 0.772 at $20^\circ/4^\circ$. The *hydrochloride* crystallises in needles melting at $247-248^\circ$; the *platinochloride* in pale yellow needles; the *carbonate* and the *nitrite* in white needles. Hexamethylenediamine nitrite is only partially decomposed when its aqueous solution is boiled. Dihydromesoanthramine nitrite yields anthracene. *Diphenylcarbinamine nitrite*, which crystallises in white needles, yields diphenylcarbinol. C. F. B.

Action of Sodium on Acetone. By P. C. FREER (*Amer. Chem. J.*, 15, 582—605).—It is proved that when metallic sodium acts on a dilute xylene solution of acetone (1 : 100), hydrogen is evolved to the extent of about 63 per cent. of the amount corresponding with the displacement of 1 atom of hydrogen by sodium. When sodium acts on pure acetone, none of this hydrogen is evolved; it is used up in reducing the acetone to isopropyl alcohol, &c.

Acetone in ethereal solution was then exposed to the action of sodium, this and other operations being carried out in an atmosphere of hydrogen. The product consisted of two parts, nearly equal in amount, and respectively insoluble and soluble in ether. The former was found to consist chiefly of acetone sodium, together with sodium isopropoxide and disodium pinaconate in about equal proportions, and a trace of sodium ethoxide. The part soluble in ether consists almost entirely of sodium acetone. *Sodium acetone* oxidises very readily, and is decomposed by cooled dilute acetic acid, yielding acetone, together with small quantities of mesitylic oxide and phorone. It appears to have the formula $\text{CH}_3\text{CMe}\cdot\text{ONa}$ (and not $\text{CH}_3\text{Na}\cdot\text{COMe}$), because, when it is treated with benzoic chloride, β -allylic benzoate, $\text{CH}_3\text{CMe}\cdot\text{OBz}$, is among the products. The product of the action is extracted successively with sodium hydrogen carbonate, carbonate, and hydroxide. The residual oil contains mesitylic oxide and ethyllic, isopropyllic, and β -allylic benzoates; when hydrolysed with

dilute hydrochloric acid, it yields benzoic acid, together with ethylic and isopropyllic alcohols and acetone; with caustic potash, no acetone is obtained, but phorone and mesitylic oxide instead. The portion soluble in sodium hydrogen carbonate contains benzoic acid. That soluble in sodium carbonate contains mono- and di-benzoylacetone, and yields acetophenone, acetic acid, and benzoic acid when distilled. The higher-boiling part of the insoluble oil contains some substances which have been isolated, but not yet identified.

C. F. B.

Electrical Conductivity of Formic acid. By V. SAPOJNIKOFF (*J. Russ. Chem. Soc.*, 25, 109—110).—As a rule, pure substances are bad conductors of electricity, but Hartwig found that formic acid conducted comparatively well. The author has repeated the experiments with as pure acid as he could obtain (m. p. 8.39°), and finds for it a conductivity only one-sixteenth of that observed by Hartwig. As this acid still contained about 0.2 per cent. of water, he is of opinion that the pure acid is practically a non-conductor.

J. W.

Oxymethylene Derivatives of Ethylic Acetoacetate, Acetylacetone, and Ethylic Malonate. By L. CRAISEN (*Ber.*, 26, 2729—2735).—When ethylic acetoacetate, or acetylacetone is heated in a reflux apparatus with ethylic orthoformate and acetic anhydride, alcohol is eliminated and ethoxymethylene derivatives are obtained. A similar condensation occurs with ethylic malonate, but the action is much slower and requires the addition of zinc chloride.

Ethylic ethoxymethyleneacetoacetate, $\text{OEt}\cdot\text{CH}\cdot\text{C}(\text{Ac})\cdot\text{COOEt}$, is a colourless oil, boils at $265\text{--}266^\circ$ under ordinary pressure, and at $149\text{--}150^\circ$ under 15 mm., and has a sp. gr. of 1.0736 at 15° . It combines with phenylhydrazine to form ethylic phenylmethylpyrazolecarboxylate, which melts at 53° . When treated with water or alcohol, it yields *ethylic hydroxymethyleneacetoacetate*. This is a colourless liquid, boils at $199\text{--}200^\circ$ under the ordinary pressure, and at 95° under 21 mm. pressure, has a sp. gr. of 1.141 at 15° , is soluble in dilute alkali carbonates, and reddens litmus paper. With copper acetate, it yields a blue, crystalline copper salt.

Ethoxymethyleneacetylacetone, $\text{C}_6\text{H}_5\text{O}_2\cdot\text{CH}\cdot\text{OEt}$, boils at $256\text{--}258^\circ$ under the ordinary pressure, and at 141° under 16 mm. pressure. *Hydroxymethyleneacetylacetone* melts at 47° , boils at $190\text{--}200^\circ$ under the ordinary pressure, and at 100° under 20 mm. pressure, and is a stronger acid than ethylic hydroxymethyleneacetoacetate.

Ethylic ethoxymethylenemalonate, $\text{OEt}\cdot\text{CH}\cdot\text{C}(\text{COOEt})_2$, is a colourless oil, boils at 280° , has a sp. gr. of 1.0855 at 15° , and is not decomposed by water at the ordinary temperature.

When ethylic acetoacetate and ethylic orthoformate are allowed to remain in contact with acetic chloride instead of being heated with acetic anhydride, a different reaction takes place, and ethylic acetate, ethylic formate, and ethylic ethoxycrotonate, $\text{OEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$, are formed. The latter melts at 31° , boils at $199\text{--}200^\circ$, and, when distilled over calcium hydroxide, yields the alcohol $\text{CH}_3\cdot\text{CMe}\cdot\text{OH}$, which boils at 62° .

Compounds containing the methenyl group CH combined with two

residues of the group $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$ are obtained by the prolonged action of ethylic orthoformate and acetic anhydride on an excess of ethylic acetoacetate or acetylacetone. These *methenyl* compounds are more easily obtained by adding the alkali salts of ethylic acetoacetate or acetylacetone to an alcoholic solution of the ethoxymethylene derivatives described above. *Diethylic methenyldiacetoacetate*, $\text{C}_8\text{H}_{12}\text{O}_5\cdot\text{CH}\cdot\text{C}_6\text{H}_5\text{O}_2$, melts at 96° . *Methenyldiacetylacetone*,



melts at 115° , and, by the withdrawal of the elements of water, yields a crystalline compound, $\text{C}_{11}\text{H}_{12}\text{O}_3$, which melts at 112° . When these methenyl compounds are treated with ammonia, they yield pyridine derivatives. Thus, diethylic methenyldiacetoacetate, when heated with ammonium acetate, yields ethylic dimethylpyridinedicarboxylate, and methenyldiacetylacetone, when allowed to remain in ammoniacal solution, yields *aa'*-diacetylutidine (m. p. $73\text{--}74^\circ$). In many cases it is unnecessary to prepare the methenyl compound; thus, ethylic dimethylpyridinedicarboxylate is obtained by heating ethylic ethoxymethyleneacetoacetate with ethylic paramidoacetoacetate.

E. C. R. :

Derivatives of Diethylic Succinosuccinate. By N. KJNER (*J. Russ. Chem. Soc.*, 25, 125—132).—Succinosuccinic acid (1 gram) was heated for six hours at 225° with hydriodic acid (15 c.c.) of sp. gr. 1.96. No hexamethylene was obtained, but a liquid boiling from 200° to 220° . Diketoexamethylene gave similar results.

Phosphorus pentachloride with diketoexamethylene in cold chloroform solution gives crystals which melt at 125.5° and have the composition $\text{C}_6\text{H}_6\text{Cl}_4$. These sublime in needles at a temperature below their melting point, and may be recrystallised from boiling alcohol. Paradichlorobenzene is formed at the same time.

When the sodium compound of diethylic succinosuccinate is boiled with ethylic chloro-formate, a substance $\text{C}_{12}\text{H}_{14}\text{O}_6(\text{COOEt})_2$ is formed, which is easily soluble in chloroform, less soluble in alcohol, and melts at 127° . It does not dissolve in alkalis, does not fluoresce, and its alcoholic solution does not colour ferric chloride. When treated with bromine, it loses 2 atoms of hydrogen, giving a compound $\text{C}_{12}\text{H}_{12}\text{O}_6(\text{COOEt})_2$, melting at 129° ; this may also be made from the sodium salt of diethylic quinonehydrodicarboxylate, by treating it with ethylic chloro-formate.

J. W.

Action of Iodic acid on Acetonedicarboxylic acid. By A. ANGELI and E. LEVI (*Gazzetta*, 23, ii, 97—100).—On treating acetonedicarboxylic acid with aqueous iodic acid, carbonic anhydride is evolved and heat is developed. The mixture is kept cool, and, after a time, *tetriodoacetone*, $\text{CO}(\text{CHI}_2)_3$, is deposited; it crystallises in beautiful, yellow needles, melting at 142° with decomposition. It is very soluble in acetone, less so in benzene, alcohol, ethylic acetate, or chloroform, but its solutions soon become coloured, owing to liberation of iodine. On distillation with hydriodic acid and a little red phosphorus, it yields acetone, iodoform, and symmetrical diiodoacetone,

but it gives no appreciable quantity of iodoform when treated with alkali carbonates. W. J. P.

Barium Antimony Tartrate. By E. MAUMENÉ (*Compt. rend.*, 117, 666—668).—The numbers obtained by Dumas and Piria, in their analyses of barium antimony tartrate, did not agree well with those calculated from the formula, and they attributed the divergences to the retention of water and the absorption of carbonic anhydride. The author points out that, according to his general laws, the formula of the salt is $C_6H_{7.75}O_{12.75}(SbO_3)_{1.17}(BaO)_{1.07}$, and that the numbers calculated from this formula ($O = 8$, $C = 6$, &c.) agree closely with the results of analysis. C. H. B.

Methylic Tartrates and Ethylic Tartrates. By J. FAYOLLAT (*Compt. rend.*, 117, 630—633).—Lithium, sodium, potassium, and ammonium methylic tartrates, and lithium, sodium, potassium, barium, and calcium ethylic tartrates, all crystallise in anhydrous crystals. Ammonium methylic tartrate crystallises with some difficulty, and is very hygroscopic. Polarimetric observations with (1) tartaric acid, (2) methylic hydrogen tartrate, (3) lithium methylic tartrate, (4) ammonium methylic tartrate, (5) sodium methylic tartrate, (6) potassium methylic tartrate, (7) ethylic hydrogen tartrate, (8) lithium ethylic tartrate, (9) sodium ethylic tartrate, (10) potassium ethylic tartrate, in aqueous solutions containing 1 gram molecule in 8000 c.c. of water, gave the following results.

	1.	2.	3.	4.	5.	6.
Observed deviation, column 20 cm. } long	+ 0.61	0.75	1.14	1.28	0.99	1.16
Specific rotatory power..... } power.....	+16.1	18.1	26.5	28.0	21.0	22.7
			7.	8.	9.	10.
Observed deviation, column 20 cm. } long			0.98	1.34	1.39	1.40
Specific rotatory power.....			21.8	28.8	27.5	21.6

It will be observed that, in each series, the deviations produced by the alkali salts are very approximately equal, which indicates a degree of dissociation practically the same for the various salts in the same series. Calcium and barium ethylic tartrates were examined in solutions containing 1 gram molecule in 16 litres, the deviations being +1.21 and +1.26, and the specific rotatory powers +24.3 and +20.3 respectively.

The solubilities of the salts in alcohol are so small that no comparative observations are possible, but the results with saturated solutions show that both the methylic tartrates and the ethylic tartrates retain their dextrogyrate character. C. H. B.

Influence of Organic Solvents on Specific Rotatory Power. By P. FREUNDLER (*Compt. rend.*, 117, 556—559).—The author has measured the specific rotatory power of propylic diacetyltartrate, dipropionyltartrate, dibutyryltartrate, di-*n*-valeryltartrate, and di-*n*-

caproyltartrate, dissolved in ether, alcohol, acetone, butyl ketone, light petroleum, carbon bisulphide, methylic alcohol, toluene, benzene, methylenic chloride, chloroform, carbon tetrachloride, ethylenic chloride, ethylenic chloride, chlorethylidenic chloride, methylenic bromide, bromoform, ethylenic bromide, propylic bromide, and methylic iodide. The results show that the nature of the solvent exerts very considerable influence on the rotatory power of the dissolved substances. The value of $[\alpha]_D$ for propylic diacetyltartrate, for example, varies from $+36.7^\circ$ in carbon bisulphide to -2.6° in bromoform, the specific rotatory power of the compound itself being $+13.4^\circ$. Similarly, the value for the di-*n*-valeryl tartrate varies from $+8.2^\circ$ in acetone to -4.7° in bromoform, the value for the salt itself being $+6.7^\circ$. On the whole, oxygen compounds have little influence, whilst haloïd derivatives and compounds of the benzene series tend to reduce the value of $[\alpha]_D$, and even to change its sign. The effect of different solvents is of the same order with all five compounds.

The changes in rotatory power may be due to (1) polymerisation of the active molecules, or (2) combination of the active substance with the solvent. Salts of the alkaloïds, for instance, are known to combine with alcohols and with benzene, and propylic tartrate forms compounds with benzene. Cryometric measurements show that in solutions in ethylenic bromide which have normal rotatory power, the molecular weight is normal; but in solutions in benzene which have much lower rotatory power, the molecular weight is considerably below the calculated value. It would seem that some change of the nature of dissociation takes place.

C. H. B.

Thiocarbamides. By H. SALKOWSKI (*Ber.*, 26, 2923).—The paper criticised by the author (this vol., i, 11) was by G. Mazzaron, not by G. Mazzara.

J. B. T.

Some Nitrogen Derivatives of the Higher Fatty Acids. By P. EITNER and H. WETZ (*Ber.*, 26, 2840—2847).—The amides of the higher fatty acids can be distilled under diminished pressure almost without decomposition, whilst that of the bibasic sebacic acid is almost completely decomposed. Lauramide boils at $199-200^\circ$ (12.5 mm.), myristamide at 217° (12 mm.), palmitamide at $235-236^\circ$, and stearamide at $250-251^\circ$ with slight decomposition, under the same pressure.

The nitriles obtained from these amides have been employed for the preparation of several classes of derivatives. The imidoethers are prepared by the action of dry hydrogen chloride on a liquid mixture of the nitrile with a molecule of isobutylic alcohol. *Laurimidoisobutyl ether hydrochloride*, $C_{18}H_{37}ON, HCl$, is a very hygroscopic, white, microcrystalline powder melting at $65-66^\circ$; it is slightly soluble in ether, readily in alcohol; in aqueous solution it soon undergoes decomposition. *Myristimidoisobutyl ether hydrochloride*, $C_{18}H_{37}ON, HCl$, has similar properties, and melts at $69-70^\circ$. *Palmitimidoisobutyl ether hydrochloride*, $C_{20}H_{41}ON, HCl$, is less soluble and less hygroscopic than the above; it melts at 73° . *Stearimidoisobutyl ether hydrochloride*, $C_{22}H_{45}ON, HCl$,

is only slightly hygroscopic, and melts at 77—78°. It is also less soluble in ether than its lower homologues. *Sebacimidoisobutyl ether hydrochloride*, $C_{18}H_{38}O_2N_2 \cdot 2HCl$, closely resembles the foregoing compound; it melts at 135° with decomposition.

From the imidoisobutyl ethers the corresponding amidine hydrochlorides may be prepared by the action of alcoholic ammonia. These compounds form fine, white plates or thin prisms, with a splendid silky lustre, and are not in the least degree hygroscopic. They form platinochlorides which crystallise from alcohol in slender, yellow needles. *Lauramidine hydrochloride*, $C_{11}H_{21}N_3 \cdot HCl$, melts at 128—129°; it is readily soluble in alcohol, slightly in water, insoluble in ether. *Myristamidine hydrochloride* is only very slightly soluble in water, and melts without decomposition at 135°. *Palmitamidine hydrochloride* is also scarcely soluble in water; it softens at 136°, and melts at 217°. *Stearamidine hydrochloride* has been previously prepared by Pinner (*Die Imidoäther und ihre Derivate*, S. 130). *Sebacamidine hydrochloride* melts at 166—167°.

Palmitamidine, $C_{16}H_{31}N_3$, prepared by the action of sodium ethoxide on an alcoholic solution of the hydrochloride, crystallises from alcohol in lustrous plates melting at 85°. It distils almost without decomposition at 194° (13 mm.).

The amidoximes corresponding with the nitriles are prepared by the usual method, and resemble one another very closely. They form white, lustrous plates or broad prisms, with a faint pink or greenish surface lustre. They are insoluble in water, very slightly soluble in ether, readily in alcohol. *Lauramidoxime* melts at 92—92·5°, *myristamidoxime* at 97°, *palmitamidoxime* at 101·5—102°, and *stearamidoxime* at 106—106·5°. It was found impossible to prepare the amidoxime of sebacic acid.

The amidoximes unite with a molecule of sulphurous anhydride when this gas is passed through their solutions in benzene. The products formed cannot be distinguished from one another by appearance. They are white, crystalline powders which decompose slowly, with loss of sulphurous anhydride; they all liquefy at about 100°, and simultaneously decompose. The derivative of palmitamidoxime was converted into an ammonium salt by the action of dry ammonia gas; it is likewise a white, crystalline powder which decomposes in the air. These acids have the general formula $NH_2 \cdot CR \cdot N \cdot O \cdot SO_3H$, and the authors propose to call them *amidoxime-sulphurous acids*.

The nitriles of the monobasic acids readily unite with hydrogen bromide. The following compounds of this class were obtained.

	M. p.
Dilaurenitrile hydrobromide, $(C_{12}H_{23}N)_2 \cdot HBr$..	75·5—76·0°
Dimyristonitrile hydrobromide, $(C_{14}H_{27}N)_2 \cdot HBr$	79·5—80·5
Dipalmitonitrile hydrobromide, $(C_{16}H_{31}N)_2 \cdot HBr$	84·0—85·0
Distearonitrile hydrobromide, $(C_{18}H_{35}N)_2 \cdot HBr$..	88·5—89·5

All these substances crystallise in colourless, narrow plates, are almost insoluble in water, readily soluble in alcohol, &c., and are not hygroscopic.

A. H.

Action of Ammonia on Ethylic 6-Ethoxycoumalin-3:5-dicarboxylate in absence of Water. By M. GUTHZEIT (*Ber.*, 26, 2795—2808).—The compound $\text{CH} \begin{smallmatrix} \text{CH:CH} \\ \text{CH-CO} \end{smallmatrix} \text{O}$ is named by v. Pech-

mann (*Abstr.*, 1891, 1460) coumalin instead of α -pyrone; the author also adopts this name. It has already been shown (*Abstr.*, 1891, 939) that when ethylic ethoxycoumalindicarboxylate is shaken with dilute aqueous ammonia, ethylic ethoxyhydroxypyridindicarboxylate is formed. If dry ammonia is passed into a solution of ethylic ethoxycoumalindicarboxylate in benzene, a substance, $\text{C}_{11}\text{H}_{13}\text{NO}_4$, isomeric with that previously described (*loc. cit.*) is precipitated. When crystallised from a boiling mixture of acetone and alcohol, it forms a bright yellow powder, becomes red at 180° , melts at 199° , and yields *aa*-dichlorodinicotinic acid (m. p. $75-76^\circ$) on treatment with phosphorus pentachloride.

When the substance melting at 199° is treated with cold dilute aqueous sodium hydroxide, or when a hot aqueous solution of it, mixed with a little alcohol, is filtered into hot aqueous sodium carbonate, a sparingly soluble sodium salt, $\text{C}_{11}\text{H}_{13}\text{NO}_4\text{Na} + \frac{1}{2}\text{H}_2\text{O}$, is obtained, together with a bitter oil. It was noticed that the longer the substance of melting point 199° is boiled with water, previously to adding the solution to sodium carbonate, the more sodium salt is obtained. The compound obtained from the sodium salt by treating it with acids melts at 199° , but, unlike the original substance, does not become suddenly red at 180° . It therefore seemed probable that the original substance underwent isomeric change on heating. To put this to the test, the crude substance from ammonia and ethylic ethoxycoumalindicarboxylate was crystallised from a large quantity of cold acetone, when a white, flocculent compound, having the same composition as the original substance, was obtained; on heating this in a capillary tube in the ordinary way, it becomes red at 180° and melts at 199° , but if the capillary tube is introduced into a sulphuric acid bath, heated to $178-179^\circ$, the compound melts to a red liquid, almost immediately resolidifies, and melts a second time at 199° . The compound melting at $178-179^\circ$ gives a yellow coloration with ferric chloride, and is very sparingly soluble in solvents, so much so that its molecular weight could not be determined by the cryoscopic method. Cold dilute alkalis dissolve it, forming a yellow solution, which, on acidification, evolves carbonic anhydride and deposits an oil; hot dilute alkalis produce the same effect, but partially convert the compound into the already mentioned sodium salt of the isomeride; whilst boiling with concentrated alkalis causes the evolution of ammonia. When either the crude substance (m. p. 199°) obtained from a boiling mixture of acetone and alcohol, or the compound prepared from the sodium salt, is recrystallised from cold acetone, an *isomeride* is obtained in the form of concentrically arranged prisms; it gradually becomes yellow when heated, melts sharply at 199° , gives a deep violet coloration with ferric chloride, is more soluble in solvents than the lower-melting isomeride, yields the sodium salt when treated with hot or cold dilute alkalis, and evolves only traces of ammonia when boiled with concentrated alkalis; a

molecular weight determination by the cryoscopic method established the formula $C_{11}H_{13}NO_6$. The silver salt is obtained as a white precipitate, stable towards light, when silver nitrate is added to a solution of the sodium salt; when heated with ethylic iodide, ethylic α -ethoxy- α -hydroxydinicotinate (m. p. 182°) is formed.

From these facts, it appears probable that the compound melting at 178 – 179° has the constitution $CH \begin{smallmatrix} \text{CH}(\text{COOEt}) \cdot \text{CO} \\ \text{C}(\text{COOEt}) - \text{CO} \end{smallmatrix} > \text{NH}$; whilst that melting at 199° has the tautomeric formula



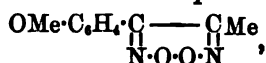
A. R. L.

Electrolytic Reduction of Aromatic Nitro-compounds. By L. GATTERMANN and K. KOPPERT (*Ber.*, **26**, 2810–2812).—A compound was obtained by the electrolytic reduction of paranitrotoluene (*Abstr.*, 1893, i, 567), which was supposed to be nitramidorthobenzyltoluene. When this compound is reduced to the diamine, the latter converted into the hydrazine, and oxidised with copper sulphate, a hydrocarbon is obtained having the same boiling point (275 – 280°) as orthobenzyltoluene.

When a mixture of paranitrobenzylic alcohol (or its acetate), paranitrotoluene, and concentrated sulphuric acid is heated at 120 – 130° , dinitrobenzyltoluene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Me} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is formed; it crystallises in yellow needles, melts at 137 – 138° , and is converted into the diamine on reduction with stannous chloride. The dihydroxy-compound obtained from this diamine is identical with that previously described (*loc. cit.*). A compound identical with the nitramidobenzyltoluene (*loc. cit.*) is obtained by heating together, at 160 – 170° , paramidobenzyl alcohol, paranitrotoluene, and concentrated sulphuric acid. These experiments, therefore, justify the assumption that, by the electrolytic reduction of paranitrotoluene, paratolylhydroxylamine is first formed, and then undergoes isomeric change into paramidobenzyl alcohol, the latter condensing with more paranitrotoluene.

A. R. L.

Action of Nitrous acid on Anethoil. By G. BOERIS (*Gazzetta*, **23**, ii, 165–194).—*Diisonitrosoanethoil peroxide*,



is prepared by the action of sodium nitrite on anethoil in acetic acid solution; it crystallises in yellow needles melting at about 97° , and was prepared by Toennies (*Abstr.*, 1881, 167) who assigned to it a constitution differing from the above. No isomeric modification seems to exist. The mononitro-derivative, $\text{C}_{10}\text{H}_9\text{N}_2\text{O}_6$, obtained by direct nitration, forms lustrous, yellow needles melting at 88 – 89° . The bromo-derivative, $\text{C}_{10}\text{H}_7\text{BrN}_2\text{O}_6$, was also prepared.

α -*Diisonitrosoanethoil*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NOH}) \cdot \text{CMe} \cdot \text{NOH}$, obtained by reducing the peroxide with zinc-dust and acetic acid, crystallises in small, lustrous prisms melting at 125° ; potassium ferricyanide reconverts it into the peroxide. Its diacetyl derivative, $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_8\text{Ac}_2$,

forms needles melting at 89° ; when dissolved in alcohol or potash, it slowly changes into diisonitrosoanethoil anhydride.

β -Diisonitrosoanethoil is obtained by heating the α -isomeride at 125° ; it melts at 206° with decomposition, and further differs from the α -compound by being very sparingly soluble in alcohol. Its diacetyl derivative forms white needles melting at 104° , and, on treatment with potash or boiling with alcohol, is reconverted into the β -dioxime; the latter is converted into the peroxide by potassium ferricyanide.

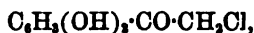
Diisonitrosoanethoil anhydride, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{N}=\text{O})_2\text{N}=\text{O}$, prepared by reducing the peroxide with tin and hydrochloric acid, crystallises in long, white needles melting at 63° ; it is soluble in alcohol or benzene, and has the normal molecular weight in freezing benzene. The mononitro-derivative is obtained by direct nitration, and forms small, lustrous crystals melting at 98 – 99° . The bromo-derivative is fairly soluble in alcohol, and crystallises in small needles melting at 73 – 74° .

α -Diisonitrosobromanethoil, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{C}(\text{NOH})\cdot\text{CMe}\cdot\text{NOH}$, is prepared by reducing the bromo-derivative of the anhydride with zinc-dust and acetic acid; it crystallises in very lustrous, small prisms melting at 143 – 144° . On heating with acetic anhydride, it yields a diacetyl derivative which forms thin needles melting at 101 – 102° , and soon decomposes in alcoholic solution, giving the bromo-derivative melting at 73 – 74° described above. The latter is also obtained on oxidising α -diisonitrosobromanethoil with alkaline ferricyanide.

β -Diisonitrosobromanethoil is prepared by heating the α -isomeride above its melting point; it forms small, white scales melting at 190° , and yields the peroxide on oxidation with alkaline ferricyanide. The diacetyl derivative is obtained in white needles melting at 130 – 131° . On reducing the β -dioxime with tin and hydrochloric acid, the same anhydride is obtained as by direct bromination of diisonitrosoanethoil anhydride.

W. J. P.

Synthesis of Ethers and Ketones from Phenols. By S. K. DZERZGOVSKY (*J. Russ. Chem. Soc.*, 25, 154–163).—Catechol and chloracetic acid in molecular proportion are melted together, and to the product phosphorus oxychloride is added in quantity equal to the weight of the chloracetic acid taken. The mixture is heated until brown and syrupy, and then treated with three times its volume of water, from which, on cooling, crystals of the chloroketone,



separate. The yield is 80 per cent. of the theoretical. The chloroketone crystallises in colourless prisms with $1\text{H}_2\text{O}$, which is given off at 110° , and melts at 173° . It is easily soluble in alcohol, chloroform, ether, benzene, and carbon bisulphide. The aqueous solution is coloured green by ferric chloride, changing to purple on the addition of sodium carbonate. It reduces silver but not cupric salts, and has an acid reaction. The diacetate is insoluble in water, but crystallises

from aqueous acetic acid in pearly scales melting at 95°. It is soluble in alcohol, ether, and chloroform. On reduction with zinc and hydrochloric acid, the chloroketone gives a theoretical yield of *aceto-catechone*, $C_6H_3(OH)_2 \cdot COMe$, which crystallises in nodular aggregates of prismatic needles. These crystals contain no water of crystallisation, melt at 116°, and are easily soluble in most solvents. The diacetate crystallises from acetic acid in colourless plates melting at 87°.

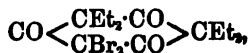
Bromaceto-catechone, $C_6H_3(OH)_2 \cdot CO \cdot CH_2Br$, crystallises with $1H_2O$, and melts at 167°.

α-Chloropropiocatechone, $C_6H_3(OH)_2 \cdot CO \cdot CHCl \cdot CH_3$, crystallises in prisms without water of crystallisation, and melts at 120°; the corresponding bromo-derivative melts at 141°.

β-Bromobutyro-catechone, $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot CHBr \cdot CH_3$, is formed in an analogous manner, but the reaction in this case is hastened by the addition of zinc chloride. It crystallises in colourless prisms without water, and melts at 135°.

Guaiacol and quinol do not give ketones when treated with chloroacetic acid and phosphorus oxychloride, but simply chloracetates. The chloracetate of guaiacol, $OMe \cdot C_6H_3 \cdot O \cdot CO \cdot CH_2Cl$, melts at 50°, and boils at 258—259°. The dichloracetate of quinol, $C_6H_3(O \cdot CO \cdot CH_2Cl)_2$, melts at 123°, and boils above 300°. J. W.

Desmotropy in Phenols : Constitution of Tetrethylphloroglucinol. By J. HERZIG and S. ZEISEL (*Monatsh.*, 14, 376—381).—When dibromotetrethylphloroglucinol (Abstr., 1890, 243) is submitted to alkaline hydrolysis, it is converted into symmetrical tetrethylacetone, monobromotetrethylphloroglucinol, and oxalic acid, with elimination of bromine and carbonic acid. The constitution of the dibromo-compound is, therefore, probably represented by the formula



and that of the phenol by the formula $CO < \begin{matrix} CEt_2 \cdot CO \\ CH \cdot C(OH) \end{matrix} > CEt_2$. The intermediate products may be either the unstable ketonic acid $CHBr_2 \cdot CO \cdot CEt_2 \cdot CO \cdot CEt_2 \cdot COOH$, or tetrethylacetone and dibromomalic acid. In either case, dibromacetic acid is formed, and this, in the presence of alkali, is immediately hydrolysed into glyoxylic acid. The latter then reduces the dibromotetrethylphloroglucinol to the monobromo-compound, and is itself oxidised to oxalic acid in the process.

The dibromotetrethylphloroglucinol (14.58 grams) is boiled for an hour in a reflux apparatus with an aqueous solution of sodium hydroxide and carbonate (8.86 and 0.25 grams in 100 c.c.) in an atmosphere free from carbonic anhydride. The product consists of a colourless, oily layer floating on a yellow, aqueous layer. The oily layer is separated and purified, and a further portion distilled from the aqueous layer. It consists almost entirely of symmetrical tetrethylacetone (Abstr., 1892, 1188), boiling at 204.9—205.9° under a pressure of 738.5 mm. The carbonic acid was estimated in a portion

of the aqueous layer, and the monobromotetraethylphloroglucinol precipitated by hydrochloric acid from the remainder, the oxalic acid being estimated in the filtrate. The monobromo-compound may be reconverted into the dibromo-compound and worked up again until the quantity is too small for treatment. JN. W.

Conversion of Allyl Compounds into Propenyl Compounds.

By A. ANGELI (*Gazzetta*, 23, ii, 101—102).—On heating saffrole at 200° with dry sodium ethoxide (5 per cent.), it is almost wholly converted into isosaffrole; this process has the great advantage of dispensing with the long heating with alcoholic potash which has hitherto been necessary for the conversion of aromatic allyl derivatives into the corresponding propenyl compounds. It is, in all probability, applicable to other similar cases. W. J. P.

Action of Nitrous acid on Unsaturated Compounds. By A. ANGELI (*Gazzetta*, 23, ii, 124—135; compare *Abstr.*, 1892, 447, 1198).—A *mononitrosite* of the composition $C_6H_5O_2N_2O_3$ is obtained on passing nitrogen trioxide through an ethereal solution of sorbic acid; it crystallises in small, white needles melting at about 110° with decomposition. Neither crotonic acid nor diallyl react with nitrous acid; stilbene, however, yields a white, crystalline substance melting at about 132° with decomposition, but no satisfactory analyses could be made.

On treating saffrole with nitrous acid in ethereal or light petroleum solution, it yields the α -nitrosite having the probable constitution



; it is a yellow powder which melts at about

130° with decomposition, and is sparingly soluble in most solvents. With piperidine, it does not give a nitrolamine, but a condensation product which forms small needles melting at 83°, and has the composition $C_{16}H_{20}N_2O_4$. On warming with phenylhydrazine, it yields a compound of the composition $C_{16}H_{17}N_2O_4$, which separates from benzene in small, yellow needles melting at 87°.

On boiling with alcoholic potash, the α -compound is converted into the isomeric β -nitrosite; this melts at 92°, and is soluble in alkalis. The author assigns to it the constitution



When warmed with concentrated hydrochloric acid, gas is evolved, and an *aldehyde*, $CH_3O_2C_6H_5 \cdot CH_2 \cdot CH(NO_2) \cdot COH$, is deposited; it crystallises in lustrous, white scales melting at 86°, and dissolves in alkalis without decomposition. Its alkaline solution readily reduces ammoniacal silver nitrate; with phenylhydrazine, it yields a *hydrazone* (?), $C_{16}H_{15}N_2O_4$, which melts at 86°. W. J. P.

β -Phenylpropylamine. By M. FREUND and E. KÖNIG (*Ber.*, 26, 2874—2875).— β -Phenylpropylamine is obtained by the reducing action

of sodium on methylbenzyl cyanide dissolved in absolute alcohol. The product is distilled with steam, dissolved in hydrochloric acid, and the solution concentrated, and extracted with ether. It is a colourless, highly refractive oil, boils at 210° (uncorr.), has a strong, basic, fishy odour, a strongly alkaline reaction, and absorbs carbonic anhydride from the air. The *hydrochloride* is extremely hygroscopic. The *platinochloride*, $(C_7H_7N)_2H_2PtCl_4$, crystallises in beautiful, lustrous, golden plates, and decomposes at about 140° . The *aurochloride* crystallises from dilute alcohol, and melts at 124° . The *picrate* melts at 182° .
E. C. R.

Oxidation of Azimidotoluene. By J. A. BLADIN (*Ber.*, 26, 2736—2738; see also Abstr., 1893, i, 375).—A small quantity of azimidobenzoic acid is obtained, together with triazoledicarboxylic acid, by the oxidation of azimidotoluene with alkaline permanganate. The two compounds are easily separated by slightly acidifying the aqueous filtrate with nitric acid and concentrating the solution on the water-bath, when the azimidobenzoic acid is precipitated.

Azimidobenzoic acid, $COOH \cdot C_6H_4 \cdot \begin{smallmatrix} N \\ \text{---} \\ NH \end{smallmatrix} N$, crystallises from acetic acid in small, colourless leaflets containing 1 mol. of acetic acid; it does not melt at 270° . The *calcium salt*, $(C_7H_4N_2O_2)_2Ca \cdot 4H_2O$, and the *barium salt*, $(C_7H_4N_2O_2)_2Ba \cdot 7H_2O$, are described.

Triazoledicarboxylic acid crystallises from water in large, monosymmetric crystals with $2H_2O$. When heated with resorcinol and zinc chloride, it yields a fluorescein which dissolves in ammonia with an intense green fluorescence. The *barium salt*, $C_3N_3H(COO)_2Ba \cdot H_2O$, is an insoluble, crystalline powder. The *copper salt* is bright blue, decomposes on heating, and is soluble in ammonia and mineral acids.

Triazole, $C_3N_3H_3$, obtained by heating the dicarboxylic acid in a current of carbonic anhydride, is a hygroscopic oil, and boils at 208 — 209° under 742 mm. pressure. The *benzoyl derivative*, $C_3N_3H_2Bz$, crystallises in long, colourless prisms, and melts at 111 — 115° .

E. C. R.

Derivatives of Thiosemicarbazide. By G. PULVERMACHER (*Ber.*, 26, 2812—2813).—By the action in the cold of alkylthiocarbimides on hydrazine hydrate in alcoholic solution, thiosemicarbazides, $NH_2 \cdot NH \cdot CS \cdot NHR'$, are formed. *Phenylthiosemicarbazide*, $NH_2 \cdot NH \cdot CS \cdot NHPh$, prepared from phenylthiocarbimide, forms six-sided prisms, and melts at 140° .
A. R. L.

Action of Acids and Acid Anhydrides on Thiocarbimides. By P. KAY (*Ber.*, 26, 2848—2852).—Krafft and Karstens (Abstr., 1892, 712) have shown that the di-acid anilides are not produced by the action of acids on the thiocarbimides, but that the mon-acid compounds are formed. The author has, however, succeeded in preparing the di-acid compounds by substituting the acid anhydrides for the acids. *Diacetylallylamine*, $CH_2 \cdot CH \cdot CH_2 \cdot N(COMe)_2$, is prepared by boiling allylic thiocarbimide with acetic anhydride, carbon oxy-

sulphide being evolved; it is a colourless liquid, boiling at 88—90° under a pressure of 14 mm. *Diacetanilide*, $\text{NPh}(\text{COMe})_2$, is obtained in a similar manner from phenylthiocarbimide. It forms crystals which melt at 37—37.5°, and is soluble in benzene, but only slightly so in cold water; it boils at 145—146° (13 mm.). *Dipropionanilide*, $\text{NPh}(\text{COEt})_2$, boils at 165—166° (17 mm.), and solidifies in colourless crystals melting at 44°. *Paratolylthiocarbimide* is prepared by boiling paratolylthiocarbimide with acetic anhydride for 3—4 minutes; it melts at 25° and boils at 245—246°. *Diacetoparatoluidide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}(\text{COMe})_2$, is produced by the further action of acetic anhydride at 170—180°, and boils at 160—161° (15 mm.). *Dibenzanilide*, $\text{NPh}(\text{COPh})_2$, is prepared from phenylthiocarbimide and benzoic anhydride. It melts at 160—161° as stated by Steiner (*Annalen*, 178, 235).

The following substances have also been prepared by this reaction, the acids and not their anhydrides being employed:—*Allylbenzamide*, $\text{COPh}\cdot\text{NH}\cdot\text{C}_3\text{H}_5$, is a colourless oil with a faint odour and bitter taste. It boils at 173—174° (14 mm.), and decomposes when heated at the ordinary pressure. It combines with bromine to form a *di-bromide*, $\text{C}_{10}\text{H}_{11}\text{Br}_2\text{NO}$, which crystallises in lustrous plates, and melts at 135°. When treated with concentrated sulphuric acid, allylbenzamide undergoes intramolecular change, and is converted into the β -methyl- μ -phenyloxazoline which has been previously described by Gabriel and Heymann (*Abstr.*, 1890, 1267); it can be very readily prepared by this means, and is also formed when a benzene solution of allylbenzamide is saturated with hydrogen chloride and heated in a sealed tube. A small amount of β -chloropropylbenzamide is also formed by this method. *Allylcinnamide*, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$, forms crystals which melt at 90—90.5°, and boils at 223—224° (14 mm.); it combines with 4 atoms of bromine and also with hydrogen chloride. Allylphthalimide, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{C}_3\text{H}_5$, is prepared from phthalic acid and thiocarbimide; it boils at 295° and melts at 70—71° as stated by Wallach and Kamenski (*Ber.*, 14, 171). *Allylsuccinimide*, $\text{C}_6\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{C}_3\text{H}_5$, boils at 130—131° (14 mm.).
A. H.

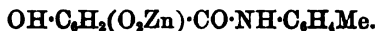
Preparation of Di-acid Anilides. By P. KAY (*Ber.*, 26, 2853—2856; compare preceding abstract). The di-acid anilides are not formed when the mon-acid derivatives are simply boiled with an acid chloride, but they may be prepared by this reaction if the mixture be heated in an oil bath to a temperature of from 170° to 200° in a flask connected with a reversed condenser. In this way, the acid chloride collects in the tube of the condenser and the anilide is acted on mainly by the superheated vapour. The reaction succeeds better when the acid chloride is gradually added as the conversion proceeds. All the di-acid anilides described in the foregoing abstract have been also prepared in this way. *Diacetorthotoluidide* is a colourless oil which boils at 145° (11 mm.), and does not solidify at the ordinary (summer) temperature.
A. H.

The Solid State of some Aldoximes. By E. BOURGEOIS and J. DAMBMANN (*Ber.*, 26, 2856—2861).—The fact that many of the
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aldoximes exist in a solid form has been observed by many chemists. α -Benzaldoxime may be obtained in a pure state by melting the almost pure material, at about 30° , maintaining it at a temperature of 26 — 27° , and introducing a crystal of the solid compound. Splendid lustrous prisms are formed, which melt sharply at 35° , and may be preserved without change. It boils at 117.5° (14 mm.). When the β -modification, melting at 125° , is slowly heated under diminished pressure, a small amount of it sublimes, but the remainder is converted into the α -form, which suddenly boils up and distils at 117.5° (14 mm.).

Isovaleraldoxime cannot be got to solidify completely. The solid substance melts at 48.5° , and the liquid thus formed boils at 164 — 165° (corr.), but does not solidify entirely when cooled; the solid matter obtained liquefies in the course of two or three days. The melting point determination is only approximate, the temperature found varying with the length of time for which the sample has been heated; this behaviour of the substance is probably due to the presence of small amounts of impurities. Solid cenanthaldoxime can be prepared much more easily in the pure state, but behaves in a similar manner to the others. It boils at 100.5° under a pressure of 14 mm., but the distillate does not completely solidify. The solid portion melts at 55.5° , and can be preserved without change. A. H.

Galloparatoluidide. By P. CAZENEUVE (*Compt. rend.*, 117, 633—635).—When equal weights of crystallised paratoluidine and gallotannic acid are heated together at about 150° for an hour, and the product is treated with dilute hydrochloric acid, and crystallised from dilute alcohol, *galloparatoluidide*, $C_6H_4(OH)_3 \cdot CO \cdot NH \cdot C_6H_4Me$, is obtained in white, crystalline plates melting at 211° , only slightly soluble in cold water, but very soluble in hot water, and soluble in alcohol and ether; the crystals contain $2H_2O$, which they lose at 100° . Galloparatoluidide is not affected by alkalis out of contact with air, even in boiling solutions, but in presence of air it is slowly oxidised. When heated with hydrochloric acid in sealed tubes at 150° , it splits up into gallic acid and paratoluidine. Galloparatoluidide yields saline derivatives analogous to those of gallanilide (*Abstr.*, 1893, i, 638). When a boiling solution is mixed with zinc acetate, it yields a very insoluble, white precipitate of the compound



Lead acetate produces a precipitate of similar constitution, and lime water and baryta water yield analogous compounds which alter when exposed to air. Mercuric and cupric acetates are reduced as with gallanilide. When boiled with nitrosodimethylaniline in presence of alcohol, gallotoluidide yields the homologue of gallic blue (*Abstr.*, 1893, i, 510).

Orthotoluidine, methylaniline, dimethylaniline, and the so-called pure xyldine of commerce yield no analogous compounds when heated with gallotannic acid. C. H. B.

Amido-amidine Bases. By E. LELLMANN and R. HAILER (*Ber.*, 26, 2759—2763).—The authors have endeavoured to determine to what extent the power of directly dyeing cotton, which is possessed by the monazo-dyes derived from dehydrothioparatoluidine, is dependent on the nature of the elements in the complex $C \begin{smallmatrix} S \cdot O \\ \diagup \quad \diagdown \\ N \cdot C \end{smallmatrix}$, and how far it is conditioned by their arrangement. *Paranitrobenzoparatoluidide*, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4Me$, prepared by heating paranitrobenzoic acid with paratoluidine for 5—6 hours at 180—220°, crystallises from glacial acetic acid in greyish-yellow, silky, lustrous needles melting at 203°. *Paranitrobenzometanitroparatoluidide*,



is formed from the preceding compound by the action of nitric acid (sp. gr. 1.45) at 0°, and crystallises from alcohol in golden-yellow plates melting at 171—172°; on reducing it with stannous chloride,

paramidobenzenyltoluyleneamidine, $NH_2 \cdot C_6H_4 \cdot C \begin{smallmatrix} NH \\ \diagup \quad \diagdown \\ N \end{smallmatrix} > C_6H_4Me$, is obtained, which crystallises from dilute ammonia in small, yellow needles, and melts at 113—114°. The *sulphate*, $C_{14}H_{13}N_3H_2SO_4 + H_2O$, is crystalline. The diazo-derivative readily dyes cotton.

Metamidobenzenyltoluyleneamidine melts at 238°, instead of at 227—229° as stated by Schack; the *sulphate*, $(C_{14}H_{13}N_3)_2H_2SO_4 + 1\frac{1}{2}H_2O$, not $C_{14}H_{13}N_3H_2SO_4$, crystallises in plates. The tinctorial power of the diazo-derivative is less marked than that of its isomeride. *Paranitrobenzometaxyliide*, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4Me_2$, is prepared by heating paranitrobenzoic acid and metaxyliide at 230°, and crystallises from alcohol in grey prisms melting at 166°. *Paranitrobenzonitrometaxyliide*, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4Me_2 \cdot NO_2$, is obtained from the preceding compound in a similar manner to the toluidide; it crystallises from glacial acetic acid, and melts at 139—140°. *Paramidobenzenyl-metaxylieneamidine*, $NH_2 \cdot C_6H_4 \cdot C \begin{smallmatrix} NH \\ \diagup \quad \diagdown \\ N \end{smallmatrix} > C_6H_4Me_2$, is formed by the reduction of the nitro-compound, and crystallises from dilute ammonia in slender, almost colourless needles melting at 183°. The *sulphate*, $C_{14}H_{13}N_3H_2SO_4 + 6H_2O$, is deposited in slender, colourless, lustrous needles. The tinctorial power of the diazo-derivative was not determined.

J. B. T.

Protocatechuic Aldehyde and Piperonal. By R. WEGSCHEIDER (*Monatsh.*, 14, 382—389).—In order to convert piperonal into protocatechuic aldehyde, it is not necessary to isolate the dichloropiperonal (compare Fittig and Remsen, *Annalen*, 159, 148). Piperonal (28 grams) is shaken with phosphorus pentachloride (120 grams) in a reflux apparatus, the temperature not being allowed to rise, and the action is completed by heating the mixture at 108—109°; the product is then treated with water (1512 c.c.), and the mixture heated, and finally boiled. The lower oily layer, which contains the protocatechuic aldehyde, is extracted with ether, and the aldehyde

thus obtained is recrystallised from toluene; the yield is 80 per cent. Opianic acid yields only 8 per cent. of protocatechuic aldehyde when boiled with hydrochloric acid, and the intermediate product, vanillin, yields 20 per cent.

Protocatechuic aldehyde melts at 153—154°. The *lead* and *mercury* compounds and the *oxime* are described. The *phenylhydrazone* exists in two, probably stereoisomeric, modifications. The first, which melts at 174—175°, is formed when cold alcoholic solutions of the aldehyde and phenylhydrazine are mixed. The second is obtained on heating the first with an alcoholic solution of phenylhydrazine, and melts at 127—128°; in contact with cold water, it is slowly transformed into the first modification.

An attempt to synthesise piperonal from protocatechuic aldehyde and trioxymethylene yielded only traces, whilst by heating the *lead* and *mercury* compounds with methylenic iodide, none was formed; when, however, the aldehyde (5 grams) was heated with methylenic iodide (14.7 grams) and alcoholic potash (6.3 grams in 10 c.c. of methylic alcohol) for 9½ hours at 100°, and then for 2½ hours at 135—140°, a small amount (0.020 gram) of piperonal was obtained (m. p. 35—36°); the piperonic acid, obtained on oxidising it with permanganate, melted at 221.5—224.5°. JN. W.

Violet Perfume. By F. TIEMANN and P. KRÜGER (*Ber.*, 26, 2675—2708).—The characteristic fragrance of violets is also possessed by dried iris root, which has been employed by the authors as the source of the fragrant oil which forms the subject of the present paper. It has been found impossible to obtain sufficient material from violet blossoms themselves to ascertain whether the odoriferous substance contained in them is or is not identical with those described.

To isolate the fragrant oil, the dried iris root is repeatedly extracted with ether, and the extracted matter then distilled with steam. The non-volatile portion consists mainly of resinous matter and a little myristic acid, irigenin, iridic acid, &c., whilst the readily-volatile fraction contains the *irone* or fragrant oil, together with a considerable amount of myristic acid and its methylic salt, oleic acid, an ethereal oleate, oleic aldehyde, and small amounts of other substances. The acids and ethereal salts are removed from the more volatile portion, obtained by the repeated fractional distillation of the oil with steam, by dissolving it in cold alcoholic potash and precipitating with water. Aldehydes are next oxidised by warming with water and silver oxide, and the *irone* finally purified by conversion into the phenylhydrazone, which is then decomposed by distillation with dilute sulphuric acid.

Irone, $C_{15}H_{20}O$, is an oil which is scarcely soluble in water, readily in alcohol, &c., boils at 144° under a pressure of 16 mm., and has a sp. gr. of 0.939 at 20°. Its index of refraction, n_D , is 1.50113, and it is dextrorotatory. The smell of the pure substance is sharp, and, in the concentrated form, quite unlike that of violets, but when largely diluted resembles that of the natural flowers. The *phenylhydrazone* is a yellowish-brown oil. The *oxime*, $C_{15}H_{20}NOH$, crystallises with

very great difficulty in lustrous, white plates melting at 121.5° , but is generally obtained as an oil. Ironone is a methyl ketone, yielding chloroform on treatment with sodium hypochlorite.

When treated with hydriodic acid and phosphorus, ironone loses a molecule of water, and forms *irene*, $C_{13}H_{18}$, which is a colourless oil boiling at $113-115^{\circ}$ (9 mm.). It has a sp. gr. of 0.9402 at 20° , and a refractive index of 1.5274. It dissolves in concentrated sulphuric acid at the ordinary temperature, decolorises a solution of bromine in acetic acid, and is gradually converted into a resin by the action of the air. When oxidised with vigorous reagents, irene is broken up into compounds containing only a small number of carbon atoms, such as formic, acetic, and pyruvic acids; but when the oxidation is more carefully conducted, a series of compounds is obtained the nature of which throws much light on the constitution of irene itself and ironone.

Oxydihydroxydehydroirene, $C_6H_5Me < \begin{smallmatrix} CMe_2 \cdot CH \cdot OH \\ CO - CH \cdot OH \end{smallmatrix}$, formed by the action of chromic acid in acetic acid solution, crystallises in highly refractive rhombohedra melting at $154-155^{\circ}$, and has feebly acid properties.

Iregenonedicarboxylic acid, $COOH \cdot CO \cdot C_6H_5 \cdot Me \cdot CMe_2 \cdot COOH$, is produced by the action of alkaline permanganate on the foregoing compound. It crystallises from hot water in short needles or oblique prisms melting at 227° .

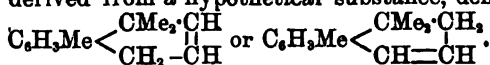
Iregenonetricarboxylic acid, $COOH \cdot CO \cdot C_6H_5 \cdot (COOH) \cdot CMe_2 \cdot COOH$, is formed by the further oxidation of the foregoing, and crystallises from water, at 5° , in granular prisms containing water of crystallisation. At 110° , the crystals become anhydrous, and melt with decomposition at 227° . The *trimethyl salt* forms compact crystals melting at $127-128^{\circ}$.

Ioniregenetricarboxylic acid, $C_6H_5(COOH)_2 \cdot CMe_2 \cdot COOH$, is the final product of the oxidation of irene, when this is carried out at first by gentle, and then by more powerful, oxidisers. It crystallises in white needles, and is slightly soluble in hot water, alcohol, and ether. At 150° it loses water, and is converted into an anhydride which is also formed when iregenonetricarboxylic acid is heated above its melting point, carbonic oxide and water being evolved. The salts of the acid, which are also formed by dissolving the anhydride in alkalis, crystallise well. The acid is very stable, and is not altered by oxidising agents or by warm concentrated sulphuric acid. The anhydride can be distilled without decomposition. The *trimethyl salt* crystallises in colourless needles melting at 93° . The *anhydride*,

$COOH \cdot C_6H_5 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > O$, crystallises from benzene in plates melting at 214° . When the ammonium salt of ioniregenetricarboxylic acid is heated in a current of carbonic anhydride, the corresponding imido-acid, $COOH \cdot C_6H_5 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > NH$, is produced. It is a white, crystalline powder which is insoluble in the usual solvents, melts above 300° , and boils a few degrees higher than this. Its *silver salt* is a white powder, which, when heated in a current of carbonic anhydride,

yields the imide of dimethylhomophthalic acid, $C_6H_4 \begin{smallmatrix} CMe_2 \cdot CO \\ CO - NH \end{smallmatrix}$, previously prepared by Gabriel (Abstr., 1887, 725).

The oxidation products of irene may therefore be looked on as derived from a hypothetical substance, dehydroirene, of the formula



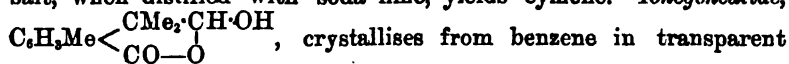
In order to throw further light on the constitution of irone and irene, a series of synthetical researches was made, starting with geranaldehyde (citral), a substance which has been shown by Semmler (Abstr., 1891, 540) to have the constitution $CHMe_2 \cdot CH_2 \cdot CH : CH \cdot CMe_2 \cdot CH \cdot COH$, since, when treated with potassium hydrogen sulphate or hydriodic acid, it is quantitatively converted into cymene.

Geranaldehyde undergoes condensation with acetone, yielding *pseudoionone*, $CHMe_2 \cdot CH_2 \cdot CH : CH \cdot CMe_2 \cdot CH \cdot CH : CH \cdot COMe$. This substance is an oil, boiling at $143-145^\circ$ (12 mm.), has a sp. gr. of 0.9044, and a refractive index of 1.5275. The *phenylhydrazone* and the *oxime* are thick oils. It does not combine with sodium hydrogen sulphite.

When *pseudoionone* is heated with dilute sulphuric acid and a little glycerol, it is converted into the isomeric *ionone*, $C_{15}H_{20}O$. This substance boils at $126-128^\circ$ at 12 mm., has a sp. gr. of 0.9351, and a refractive index of 1.507, and is optically inactive. It has a characteristic odour resembling that of violets, and, at the same time, that of the vine blossom. When heated with hydriodic acid and phosphorus, it loses water, and yields *ionene*, $C_{15}H_{18}$, which boils at $106-107^\circ$ (10 mm.), has a sp. gr. of 0.9338, and a refractive index of 1.5244. It resembles irene very closely, and, like it, has the properties of a terpene. When cautiously oxidised with chromic acid, it yields a mixture of the following compounds, which can be separated by means of their calcium salts.

Ionogenonic acid, $C_6H_4 \cdot Me \begin{smallmatrix} CMe_2 \\ CO \end{smallmatrix} > CH \cdot COOH$, forms white needles melting at 237° .

Ionegenedicarboxylic acid, $COOH \cdot C_6H_4 \cdot Me \cdot CMe_2 \cdot COOH$, forms vitreous prisms readily soluble in alcohol, &c., but only slightly in boiling water. When rapidly heated, it melts at $130-131^\circ$, but when gradually heated at a few degrees lower, it is converted into the *anhydride*, which crystallises from light petroleum in long, white needles melting at 105° . The acid is bibasic, and its calcium salt, when distilled with soda lime, yields cymene. *Ionegenealide*,



plates melting at 175° . This substance possesses feeble acid properties, and has the composition of the semi-aldehyde of *ioneenedicarboxylic acid*. It does not, however, appear to contain the aldehyde group, and is therefore probably an anhydride of the constitution shown. It is very readily converted by oxidation into *ioneenedicarboxylic acid*.

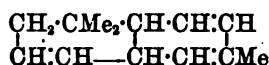
Ionene is converted, by oxidation with alkaline permanganate, into

ionegenetricarboxylic acid, $C_8H_8(COOH)_2 \cdot CMe_2 \cdot CO \cdot COOH$, which crystallises with $2H_2O$. When rapidly heated, it melts at $140-145^\circ$, and decomposes above this temperature, the anhydride of ioniregenetricarboxylic acid being formed. The final product of the oxidation of ionene itself, and of the oxidation products just described, is ioniregenetricarboxylic acid, identical with that obtained from irene.

The isomeric hydrocarbons, irene and ionene, are shown by the nature of their oxidation products to be trimethyl derivatives of a tetrahydronaphthalene. They both contain three ethylene linkings (refractive index), of which two are probably in the ring which by the removal of two hydrogen atoms is converted into the benzene ring, as this is necessary to account for the terpene-like properties of the two substances. The constitution of ionene follows from that of ionone, which is shown, by its formation from pseudoionone by intramolecular change, to be probably



I. Ionone.

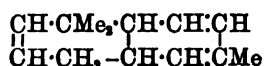


II. Ionene.

Ionene therefore has the formula II, whilst the constitution of the isomeric irene is most probably represented by IV. Irone is related to irene in the same way as ionone to ionene, and therefore has the formula III,



III. Irone.



IV. Irene.

Ionone and irone are both without injurious effect on the animal organism. The odours of ionone and irone are extraordinarily alike, and can only be distinguished by observers of great experience, and this is looked on by the authors as an additional confirmation of the great similarity in constitution of the two compounds.

It is probable that either irone, ionone, or some optically isomeric substance is present in the blossoms of the violet, but this question has not yet been decided experimentally.

A. H.

Compounds of the Geranialdehyde (Citral) Series. By F. TIEMANN and F. W. SEMMLER (*Ber.*, 26, 2708—2729).—Geranialdehyde (citral), $CHMe_2 \cdot CH_2 \cdot CH \cdot CH \cdot CMe \cdot CH \cdot COH$ (Abstr., 1891, 539), is converted, by careful reduction with sodium and alcohol, into optically inactive geraniol, $CHMe_2 \cdot CH_2 \cdot CH \cdot CH \cdot CMe \cdot CH \cdot CH_2 \cdot OH$, and can be obtained from the latter by oxidation (Abstr., 1891, 30). Several substances of the formula $C_{10}H_{18}O$ isomeric with geraniol are known. Among these are coriandrol, which is dextrorotatory (Abstr., 1891, 540); rhodinol, feebly laevorotatory (Abstr., 1892, 203); and linalool. The rotation of the last of these compounds varies with the origin of the substance, but it is probable that the compounds described as aurantiol, lavendol, nerolol, and linalool (Abstr., 1892, 868, 1236) are in reality identical, the slight differences observed between them

being due to accidental impurities. All these compounds of the formula $C_{10}H_{18}O$, as well as geraniol, are converted by cautious oxidation into geranaldehyde. In order to account for the existence of these optically active forms isomeric with geraniol, it is necessary to assume that they have a different structural formula from the latter, such as $CH_3 \cdot CMe \cdot CH \cdot CH \cdot CH \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot OH$ or



and that on oxidation a change in the position of the ethylen linking, analogous to that observed by Fittig, takes place.

Geranaldoxime, $C_{10}H_{17}NOH$, is a yellow oil, boiling at $143-145^\circ$ (12 mm.), and has a sp. gr. of 0.9386 at 20° and a refractive index $[n]_D$ of 1.51433. When distilled at the ordinary pressure, the corresponding nitrile is formed. *Geranalphenyldrazone*, $C_{10}H_{15}N_2HPh$, is a red oil which cannot be distilled. *Geranalanilide*, $C_{10}H_{15}NPh$, is obtained by heating the constituents together at 150° . It is a yellow oil boiling at 200° (20 mm.).

Geranionitrile, $C_9H_{15}CN$, is prepared by heating geranaldoxime with acetic anhydride. It is a colourless liquid which boils at 110° (10 mm.), has a sp. gr. of 0.8709 at 20° , and a refractive index of 1.4759. When digested with an alcoholic solution of hydroxylamine, an oily amidoxime is formed.

Geranic acid, $C_9H_{15}COOH$, can be obtained from the nitrile by the action of alcoholic potash much more readily than by the oxidation of geranaldehyde with silver oxide (Abstr., 1891, 323). It is an oil, boils at 153° (13 mm.), has a sp. gr. of 0.964 at 20° , and a refractive index of 1.4797. Its odour resembles that of the higher fatty acids.

When geranaldehyde is carefully oxidised with chromic acid at a low temperature, an uncrystallisable acid of the formula



is obtained, together with methyl hexylene ketone. The same products are obtained, under the same conditions, from geraniol.

Methylhexylenecarbinol, $CHMe \cdot CH_2 \cdot CH \cdot CH \cdot CHMe \cdot OH$, is formed, together with geranic acid and methyl hexylene ketone, in the hydrolysis of geranionitrile. It boils at 175° , has a sp. gr. of 0.8545 at 20° , and an index of refraction of 1.4505. This substance is identical with the compound previously prepared by Wallach by the reduction of methyl hexylene ketone (Abstr., 1893, i, 598).

Methyl hexylene ketone, $CHMe \cdot CH_2 \cdot CH \cdot CH \cdot CMe$, has been previously described by Wallach (Abstr., 1890, 1314). The formula ascribed above to this compound differs from that proposed by Wallach, $CHMe \cdot CH \cdot CH \cdot CH_2 \cdot CMe$. The authors point out that their formula explains the various reactions of the compound, and is, moreover, in agreement with the formulae of the other compounds derived from geranaldehyde; they propose to examine the question further.

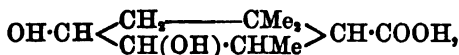
Methyl hexylene ketone is converted by the action of bromine and soda into tribromomethylhexylcarbinol, $C_9H_{11}Br_3O \cdot OH$, which separates from light petroleum in snow-white crystals melting at $98-99^\circ$.

Geraniolene, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$, is formed when geranic acid is distilled at the ordinary pressure, carbonic anhydride being evolved. It boils at $142\text{--}143^\circ$, has a sp. gr. of 0.757 at 20° , and a refractive index of 1.4368. It combines with 4 atoms of bromine, forming an oily additive compound, $\text{C}_9\text{H}_{16}\text{Br}_4$.

Geranic acid, its nitrile, and geraniolene are, like pseudoinone (see preceding abstract), converted into cyclic compounds of the same molecular weight by the action of dilute acids.

Isogeranic acid, $\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}\cdot\text{CHMe} \end{smallmatrix}\text{CH}\cdot\text{COOH}$, is obtained by shaking the oily geranic acid with 65 per cent. sulphuric acid. It crystallises from water or light petroleum in white needles melting at 103.5° , and is only slightly soluble in hot water, readily in alcohol and ether. It boils at 138° (11 mm.), and can also be distilled without decomposition at the ordinary pressure. The *dibromide* is formed by the direct addition of bromine, using a solution in chloroform. It separates from light petroleum in white crystals melting at 121° .

Dihydroxydihydroisogeranic acid,



is formed by the action of potassium permanganate on a solution of the acid in sodium carbonate. It separates from absolute alcohol in well-developed crystals melting at $195\text{--}196^\circ$.

Isogeranionitrile, $\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}\cdot\text{CHMe} \end{smallmatrix}\text{CH}\cdot\text{CN}$, is formed from the nitrile of geranic acid by the action of 70 per cent. sulphuric acid. It boils at $87\text{--}88^\circ$ (11 mm.), has a sp. gr. of 0.9208 at 20° , and an index of refraction of 1.4734. When the nitrile is hydrolysed, isogeranic acid is obtained. The *amidoxime* of the nitrile is solid, and melts at 165° .

Isogeraniolene, $\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}\cdot\text{CHMe} \end{smallmatrix}\text{CH}_2$, is produced in a similar manner from geraniolene; it boils at $138\text{--}140^\circ$, has a sp. gr. of 0.7978 at 22° , and an index of refraction of 1.4434.

It will be observed that all the cyclic isomerides have a lower boiling point, higher sp. gr., and somewhat lower index of refraction than the corresponding members of the geranaldehyde series.

A. H.

Synthesis of Aromatic Hydroxyketones. By M. NENCKI (*J. Russ. Chem. Soc.*, 25, 110—124).—Zinc chloride (15 grams) is dissolved in glacial acetic acid (40 grams), and to the solution dry gallobenzophenone (10 grams) is added, the mixture being heated on the water bath in a flask connected with a reflux condenser until the ketone is completely dissolved. Phosphorus oxychloride is then added drop by drop, and after 10 minutes' heating the mixture is poured into cold water. Recrystallisation from boiling alcohol gives rhombic needles which melt at 165° . The substance is a double ketone, $\text{COPh}\cdot\text{C}_6\text{H}_4(\text{OH})_2(\text{OAc})\cdot\text{COPh}$, whose monophenylhydrazone melts at $248\text{--}249^\circ$.

Hydrolysis of the compound $\text{C}_{17}\text{H}_{14}\text{O}_6$, by means of 70 per cent.

sulphuric acid, yielded the compound $\text{COPh} \cdot \text{C}_6\text{H}(\text{OH})_2 \cdot \text{COMe}$; this gives a diphenylhydrazone melting at 233—234°.

Chloracetic acid and phenol, with phosphorus oxychloride, or zinc chloride, give the ethereal salt $\text{CH}_2\text{Cl} \cdot \text{COOPh}$ (m. p. 44°). Pyrogallol behaves differently from phenol, giving, with phosphorus oxychloride and chloracetic acid, the ketone $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$. This gallochloracetophenone melts at 167—168°, is easily soluble in alcohol, ether, and boiling water, but only sparingly in cold water. Phenylhydrazine gives a hydrazone-hydrazide, $\text{C}_{20}\text{H}_{20}\text{O}_2\text{N}_4$, which melts at 197—198°. Aniline gives the compound



which melts at 132°, and may be recrystallised from alcohol or boiling benzene. Caustic alkalis or calcium carbonate give the oxide $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{C} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix} \text{CH}_2$ soluble in boiling water, and melting at 224°.

Gallobromacetophenone may be obtained by using bromacetic instead of chloracetic acid. It melts at 159°. J. W.

Dimethylamidobenzoic acids. By C. LAUTH (*Compt. rend.*, 117, 581—583).—*Orthodimethylamidobenzoic acid* is obtained by the action of methylic iodide on a hot alcoholic solution of sodium orthamidobenzoate. It crystallises in long needles melting at 175°, dissolves in 500 parts of cold water, and is very soluble in alcohol, ether, and benzene, forming solutions which have a blue fluorescence. It combines with both acids and alkalis, forms no nitroso-compound, but yields yellow, orange, or brown colouring matters with diazo-derivatives. When treated with oxidising agents, and especially with cupric chloride or chloranil, it yields a reddish-violet colouring matter, $\text{COOH} \cdot \text{C}_6\text{H}_2(\text{NH}_2)_2 \cdot \text{C}(\text{OH})[\text{C}_6\text{H}_2(\text{NMe}_2)_2 \cdot \text{COOH}]_2$, which has the general properties of triphenylmethane derivatives, together with special properties resulting from the presence of the COOH group; it is soluble in alkalis, and is precipitated from its solutions by acids, dyes metallic mordants, and also dyes wool and cotton mordanted with tannin, in the same way as basic colouring matters.

Orthodimethylamidobenzoic acid condenses with tetramethyldiamidobenzhydrol, and, after oxidation with lead peroxide, yields a blue-violet monocarboxyhexamethylrosaniline. With benzaldehyde or metanitrobenzaldehyde, it yields a beautiful blue colouring matter, $\text{OH} \cdot \text{CPh}[\text{C}_6\text{H}_2(\text{NMe}_2)_2 \cdot \text{COOH}]_2$, which dissolves in alkalis, and dyes wool and mordanted cotton.

Paradimethylamidobenzoic acid is obtained in a similar manner. It yields no colouring matter when oxidised, and with condensing reagents, it yields hexamethylrosaniline-violet and malachite-green, which do not contain the carboxyl group.

Metadimethylamidobenzoic acid, prepared in a similar way, or by transforming Griess' benzobetaïne, yields no colouring matters, either with oxidising or with condensing reagents.

It would seem that the introduction of the group COOH into

dimethylaniline, and the orientation of this group with respect to the NH_2 group, confers peculiar properties on each of the three isomerides, and determines whether, on oxidation or condensation, they will yield colouring matters containing the carboxy-group, colouring matters not containing this group, or no colouring matters at all.

C. H. B.

Ethereal Salts of Anhydrohippuric acid. By F. WEISS (*Ber.*, 26, 2641—2645).—The phenylic anhydrohippurate obtained by the action of phosphorus oxychloride on phenylic hippurate is found by the cryoscopic method to have the formula assigned to it (*Abstr.*, 1893, i, 579); the constitutional formula which best explains its

behaviour is $\text{NBz} \begin{smallmatrix} \text{CH} \\ \diagup \diagdown \\ \text{COPh} \end{smallmatrix}$. It combines with 2 atoms of chlorine

forming a compound which readily loses hydrogen chloride. If treated with phosphorus pentachloride, the product, on hydrolysis with water, yields *phenylic hydroxyhippurate*, $\text{NHBz} \cdot \text{CH}(\text{OH}) \cdot \text{COOPh}$, which melts at 170° , and when heated with alkalis decomposes into benzamide, phenol, and glyoxylic acid. The homologous compound $\text{NHBz} \cdot \text{CMe}(\text{OH}) \cdot \text{COOPh}$ (from phenylic anhydro- α -benzoylamidopropionate) melts at 134° . If the hydroxyl group in these compounds were replaced by the group SPh , derivatives of the mercapturic acids would be obtained.

A. R. L.

Hexahydrosalicylic acid. By A. EINHORN and R. WILLSTÄTTER (*Ber.*, 26, 2913—2914).—By the action of sodium on salicylic acid in amylic alcoholic solution *hexahydrosalicylic acid*,



is formed, together with a mixture of various other acids which have not been investigated. It is readily soluble in water, and crystallises in prismatic needles, or tetragonal plates, melting at 105° . The acid gives no coloration with ferric chloride, and, in alkaline solution, decolorises potassium permanganate slowly; it boils without decomposition under the ordinary pressure, and the odour of the vapour resembles that of the higher fatty acids; the crystals are odourless. Anthranilic acid, on reduction in a similar manner, yields hexahydrosalicylic acid and ammonia. The *methylic salt* is a colourless liquid, with an ethereal fruity smell; it boils without decomposition, and gives no coloration with ferric chloride.

Metahydroxybenzoic acid yields two acid reduction products; both crystallise readily, and melt at 112 — 114° and 130° respectively. Paramidobenzoic acid and dimethylparamidobenzoic acid are converted on reduction into a crystalline acid which melts at about 40° . β -Naphtholcarboxylic acid yields an acid melting at 141° . Thymotic acid has also been reduced in the same manner.

By the action of sodium on tetrahydroparatoluic acid dissolved in ethylic alcohol, *hexahydroparatoluic acid* is formed; it is liquid at ordinary temperatures, and boils at 245 — 248° . The *amide* melts at 195° . α -Bromohexahydroparatoluic acid melts at 94° , and on treatment with quinoline, yields tetrahydroparatoluic acid (m. p. 47°).

The authors points out that v. Baeyer (1879) was the first to employ sodium as a reducing agent in ethylic, or amylie alcoholic solution, and therefore that the method should bear his name rather than Wischnegradsky's, Ladenburg's, or Bamberger's.

J. B. T.

Canalgre Tannin. By H. TRIMBLE and J. C. PEACOCK (*Pharm. J. Trans.*, 53, 42—45).—Canaigre is the tuberous root of *Rumex hymenosepalus*, growing abundantly in the sandy soil of Texas, New Mexico, and Arizona. The green roots contain 11.46 per cent. tannin (by hide) of 71 per cent. purity. The paper describes in detail the extraction of the tannin, its chemical characteristics, and behaviour with various reagents. The results indicate that this tannin belongs to the group of which those from mangrove and rhatany are typical examples.

R. R.

Hydroxy- β -phenylcoumarin. By S. v. KOSTANECKI and C. WEBER (*Ber.*, 26, 2906—2908).—Metadihydroxy- β -phenylcoumarin is not obtained when phlogluinol and ethylic benzoylacetate are treated with concentrated sulphuric acid. Ethylic benzoylacetate, however, easily condenses with pyrogallol in the presence of sulphuric acid, and yields β -phenyldaphnetin, $C_{15}H_{10}O_4$; this crystallises with $1H_2O$ in long, lustrous, yellowish needles, loses its water at 100° , and then melts at 190 — 192° . It gives a red solution with alkalis, and with ferric chloride a green coloration which turns red on the addition of soda. Ammoniacal silver solution is easily reduced by it with formation of a mirror. The diacetyl compound crystallises in broad, white needles, and melts at 133 — 134° .

Metadihydroxy- β -phenylcoumarin, $C_{15}H_{10}O_4$, is obtained by warming ethylic benzoylacetate with phlorogluinol and zinc chloride on the water bath. It crystallises in colourless needles, melts at 234 — 235° , is indifferent to mordants, and reduces ammoniacal silver solution. It gives an intense yellow solution with alkalis, and a dirty violet coloration with ferric chloride. It is evidently not identical with chrysin. The diacetyl compound crystallises in white, prismatic needles, and melts at 180 — 181° .

E. C. R.

Conversion of Diphenylsulphone into Diphenylic Sulphide and Diphenylic Selenide. By F. KRAFFT and W. VORSTER (*Ber.*, 26, 2813—2822).—Diphenylsulphone melts at 128° , and boils at 232.5° (18 mm.). When a mixture of diphenylsulphone and sulphur is heated to its boiling point, sulphurous anhydride, diphenylic sulphide, and diphenylic bisulphide pass over. The bisulphide is formed by the action of sulphur on the monosulphide, and when heated with phenylsulphone, it is converted into the monosulphide. The yield of the bisulphide may, therefore, be reduced to a minimum by the following method:—The mixture (above mentioned) is heated in a retort until sulphurous anhydride ceases to be evolved, the cause of which is that the boiling point of the diphenylic sulphide (292°), which then forms the main portion of the product, is below the temperature at which the reaction takes place. The phenylic

sulphide is now distilled off, and the residue subsequently reheated, when the bisulphide reacts with the sulphone, producing more monosulphide. Diphenylic sulphide boils at 157—158° (16·5 mm.), and its sp. gr. at 15·2° is 1·1175.

ββ-Dinaphthyl sulphide is obtained from *ββ*-dinaphthylsulphone (m. p. 177°) and sulphur. Dipara- and dimeta-tolylsulphone do not react in the same manner as the above-mentioned sulphones.

Phosphorus in either of its forms appears not to interact with diphenylsulphone even at 250°.

When diphenylsulphone is heated with red selenium, the latter is first converted into the grey modification, which subsequently dissolves in the fused sulphone; if the product is distilled, after the evolution of sulphurous anhydride has ceased, *diphenylic selenide*, Ph_2Se , passes over. On reheating the residue and again distilling, a further quantity of diphenylic selenide is obtained. It is a colourless, highly refractive oil, resembling the sulphide, boils at 301—302° under ordinary pressure, and at 167° under a pressure of 16·5 mm. Its sp. gr. at 15·2° is 1·3561. Negative results were obtained with diphenylsulphone and tellurium.

Diphenylic sulphide forms a dibromo-substitution derivative, but when bromine is added to a cold ethereal or alcoholic solution of diphenyl selenide, a *dibromo*-additive compound, Ph_2SeBr_2 , separates as an orange-red, crystalline precipitate which melts at 140° with decomposition. When the dibromide is boiled with alcohol or water, or, preferably, gently warmed with 15 per cent. sodium hydroxide, *diphenylic selenoxide*, Ph_2SeO , is formed. It is a white substance which, when dried in a vacuum, melts at 113—114°. If heated in a tube over a direct flame, slight detonation accompanied by a reddish flash occurs, and an oil is formed; when a small quantity is distilled under diminished pressure, diphenylic selenide passes over. Diphenylic selenoxide yields a *dichloride*, Ph_2SeCl_2 , when treated with hydrochloric acid; it melts at 179—180°.

Experiments made with the object of preparing a selenone by oxidising diphenylic selenide with potassium dichromate showed that diphenylic selenoxide is obtained under these circumstances.

When diphenylsulphone is dissolved in hot xylene, and sodium is added, benzenesulphinic acid and diphenyl are formed. To isolate the sulphinic acid, the product is shaken with water, the aqueous solution of the sodium salt concentrated in an atmosphere of carbonic anhydride, and hydrochloric acid added in the cold, when the sulphinic acid separates.

A. R. L.

Action of Sulphuric Anhydride on Nitriles. By P. EITNER (*Ber.*, 26, 2833—2839; compare *Abstr.*, 1892, 713).—Sulphuric anhydride combines with acetonitrile to form an additive product of the formula $3\text{MeCN}\cdot 2\text{SO}_3$, which is a very hygroscopic, sandy, yellow mass, readily soluble in water, insoluble in all indifferent solvents. The *hydrate*, $3\text{MeCN}\cdot 2\text{SO}_3 + \text{H}_2\text{O}$, is precipitated as a white, flocculent mass on adding alcohol and ether to an aqueous solution of the substance. Its solution is strongly acid, but definite salts have not been obtained.

When fuming sulphuric acid is substituted for the sulphuric anhydride, an additive compound of the formula $2\text{MeCN}\cdot\text{SO}_3$, is obtained as a yellow, crystalline mass, which combines with H_2O . The substance thus formed is analogous to that obtained in a similar manner from benzonitrile, and is therefore probably *acetylsulphacetamidinic acid*, $\text{COMe}\cdot\text{NH}\cdot\text{CMe}\cdot\text{N}\cdot\text{SO}_3\cdot\text{H}$. This formula is confirmed by the fact that the aqueous solution of the compound, after a time, contains diacetamide, $\text{NH}(\text{COMe})_2$, and amidosulphonic acid, $\text{NH}_2\text{SO}_3\cdot\text{H}$.

Paratoluenitrile is converted by the action of sulphuric anhydride into *paratoluylsulphoparatolenylamidinic anhydride*,



It is a yellow, sandy mass, which is scarcely hygroscopic, and crystallises from benzene in colourless, lustrous prisms, containing $\frac{1}{2}$ mol. benzene; it turns yellow at 145° , and melts at $161.5\text{--}162^\circ$. When treated with concentrated sulphuric acid, it is decomposed with formation of imidodiparatoluylamide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{NH}$, and finally of diparatoluylamide, $\text{NH}(\text{CO}\cdot\text{C}_6\text{H}_4\text{Me})_2$. When its solution in benzene is digested with water and alcohol, ethylic paratoluate and *sulphoparatolenylamidinic acid*, $\text{SO}_3\cdot\text{H}\cdot\text{N}:\text{C}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\text{Me}$, are produced. The latter is a white powder, which does not undergo alteration in the air, crystallises from water or alcohol in prisms, and melts at $250\text{--}251^\circ$. The *barium salt* crystallises in splendid, colourless prisms.

When sulphoparatolenylamidinic acid is treated with dilute sulphuric acid, it is decomposed into sulphuric acid and the corresponding *amidine*, $\text{HN}:\text{C}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\text{Me}$, which is obtained in the form of the *acid sulphate*. This salt forms fine, white plates, melts at $240\text{--}241^\circ$, and is readily soluble in water and alcohol, almost insoluble in ether.

Paratoluenitrile therefore behaves towards sulphuric anhydride in a manner precisely similar to benzonitrile. A. H.

2' : 3'-Diphenylindoles. By F. R. JAPP and T. S. MURRAY (*Ber.*, 26, 2638—2641).—The authors observed that 2' : 3'-diphenylindoles are formed by heating to its boiling point a mixture of benzoïn with an excess of a primary aromatic amine in presence of zinc chloride, and in this way they had prepared a number of these compounds, which were, however, in the meantime, described by Bischler and Firemann (*Abstr.*, 1893, i, 519), the latter having obtained them by heating desyl anilide or desyl bromide with an aromatic amine. The authors show that desyl anilide (*loc. cit.*) and Voigt's anilbenzoïn (*J. pr. Chem.*, 31, 544; 34, 2) are one and the same substance; it melts at $98\text{--}99^\circ$.

Indole derivatives are only obtained from desyl anilide and an amine in presence of a trace of desyl bromide; they are formed, however, when desyl bromide is heated with an amine, a fact which indicates that the eliminated hydrogen bromide effects the condensation of the initially formed desyl anilide. The authors then found

that indole derivatives are obtained by heating desyl anilide with a mixture of an amine and its hydrochloride, which led to the discovery that by boiling benzoin with a mixture of an amine and its hydrochloride, a much better yield of indole derivative is obtained than by the use of zinc chloride (see above). The zinc chloride method is, however, the better one for the preparation of 2' : 3'-diphenyl- β -naphthindole, because of the tendency to form β -dinaphthylamine (Bischler and Fireman, *loc. cit.*).

2' : 3'-Diphenylorthotolindole (*loc. cit.*) melts at 135—136° (not 128°).

2' : 3'-Diphenyl- α -naphthindole, $C_{10}H_7 \begin{smallmatrix} \text{CPh} \\ \text{NH} \end{smallmatrix} > \text{CPh}$, forms colourless needles, and melts at 141°.

The compounds prepared by Lachowicz (this vol., i, 39) by the action of aniline hydrochloride and its analogues on benzoin at 160° are probably the intermediary substances in the formations of indoles.

A. R. L.

2 : 3-Hydroxynaphthoic acid. By S. v. KOSTANECKI (*Ber.*, 26, 2897—2900).—Phenylazohydroxynaphthoic acid [$\text{PhN}_2 : \text{OH} : \text{COOH} = 1 : 2 : 3$] is obtained from the hydroxy-acid in the usual way. It crystallises in reddish-brown needles, melts at 232°, and only yields pale colours with mordants after some time, probably on account of the insolubility of the dye.

Nitrosahydroxynaphthoic acid crystallises in red tablets, melts at 185° with decomposition, gives a brownish-yellow coloration with concentrated sulphuric acid, and a beautiful green with iron mordants, which is, however, unstable to boiling soap solution.

Naphthalenedioximeanhydridecarboxylic acid, $\text{COOH} \cdot C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} > \text{O}$, is obtained by heating the above nitroso-compound with hydroxylamine hydrochloride and alcohol in a reflux apparatus. It crystallises in white needles, melts at 294°, and sublimes without decomposition. When boiled with excess of alkali or with 50 per cent. sulphuric acid, it is converted into naphthalenedioxime anhydride, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} > \text{O}$ (Goldschmidt and Schmid, *Abstr.*, 1884, 1327), which crystallises in needles, and melts at 78°. The formation of this compound proves that the hydroxynaphthoic acid melting at 216° is the 2 : 3-compound.

E. O. R.

Ethereal Salts of Sulphonic acids. By F. KRAFFT and A. ROOS (*Ber.*, 26, 2823—2829).—It has been already shown (*Abstr.*, 1892, 1219) that alkyl sulphonates are produced by the action of aromatic sulphonic chlorides on alcohols in the cold. The authors now find that when the sulphochlorides are heated with the alcohols in sealed tubes, the sulphonic acids and the ethers corresponding with the alcohols are formed. Alkyl chlorides are also obtained, due apparently, not to a direct decomposition, but to the reaction between the hydrogen chloride directly formed and the alcohol. The authors confirm Armstrong and Rossiter's observation (*Proc.*, 1891, 184) with regard to the action of alcohol on 1 : 4-dibromonaphthalene-sulphonic chloride. When the latter is heated on the water-bath

with an excess of alcohol, it is entirely converted after a short time into the free sulphonic acid. That hydrogen chloride plays no important part in the change, is shown by the fact that when ethylic 1 : 4-dibromonaphthalenesulphonate is heated with absolute alcohol in a sealed tube, the products are the free sulphonic acid and ethylic ether.

A. R. L.

Thionaphthens. By L. GATTERMANN and A. E. LOCKHART (*Ber.*, 26, 2808—2809).—*Thionaphthen*, $C_6H_4<\overset{CH}{S}>CH$, is obtained by adding a solution of the diazo-derivative of orthamidochlorocinnamene, $NH_2 \cdot C_6H_4 \cdot CH:CHCl$, to one of potassium xanthate in the cold, whereby the diazoxanthate separates; if the product be warmed on the water bath, nitrogen is evolved and an oil, probably $OEt \cdot CS \cdot S \cdot C_6H_4 \cdot CH:CHCl$, is formed. When this oil is boiled for several hours with alcoholic potash, it yields thionaphthen, together with other compounds; a cold alcoholic solution of picric acid is now added to the mixture, whereby the sparingly soluble picrate of thionaphthen separates in golden-yellow needles; it melts at 149° , and on decomposition with ammonia, yields thionaphthen. The latter is driven over with steam, and forms colourless plates, melts at $30-31^\circ$, resembles both naphthalene and naphthylamine in odour, and gives a red coloration with concentrated sulphuric acid.

A. R. L.

Orientation in the Terpene Series. By A. BAEYER (*Ber.*, 26, 2861—2869).—Cases of cistrans-isomerism have not hitherto been observed in the terpene series, although the study of the hexahydrophthalic acids has rendered their existence probable. The author has found that the dihydrochloride and dihydrobromide of dipentene and terpin itself do exist in two forms, the series of lower melting point being looked upon by him provisionally as the *cis*-form.

Dipentene cis-dihydrochloride is formed when cineol or eucalyptol is treated with hydrogen chloride at the temperature of melting ice. It is a white, camphor-like mass, and melts at about 25° , whilst the already known *trans*-form melts at 50° (Wallach).

Dipentene cis-dihydrobromide is prepared by treating eucalyptol with a solution of hydrogen bromide in acetic acid at 0° . A mixture of the two isomerides is obtained from which the separate compounds may be isolated by dissolution in alcohol, and fractional precipitation with water. The *cis*-form crystallises in pointed plates melting at about 39° , whilst the already known *trans*-form crystallises in rhombic tablets, and melts at 64° .

The relative proportion of these two dihydrobromides formed by the treatment of the various compounds of the series with hydrogen bromide or phosphorus tribromide is shown in the following table.

		Dihydrobromide.	
		cis-	trans-
1. trans-Terpin	+ HBr	—	almost exclusively
2. Terpeneol cryst.	+ HBr	—	"
3. cis-Terpenhydrate	+ HBr	—	"

		Dihydrobromide.	
		cis-	trans-
4. cis-Terpin	+ HBr	a little	much
5. Limonene	+ HBr	a little	much
6. cis-Terpin	+ PBr ₃	about half	about half
7. Cineol	+ HBr	the greater portion	a little

Both forms yield the same dipentene, but different terpins. The *cis*-dihydrobromide, when treated successively with silver acetate and alcoholic potash, gives the well-known terpin, the hydrate of which melts at 117.5°. The *trans*-dihydrobromide, on the other hand, when similarly treated, gives a new *trans*-terpin, which crystallises without water and melts at 156–158°. It is readily soluble in alcohol, but only slightly in water, ether, or ethylic acetate, from which it separates in short prisms or six-sided tablets, with a strong, vitreous lustre. It boils at 263–265°, whilst Wallach found that the old *cis*-terpin boils at 258.5°. Since cineol yields almost exclusively the *cis*-dihydrobromide, it is most probably itself a *cis*-derivative, and the anhydride of the previously known *cis*-terpin. A *trans*-cineol has not yet been obtained.

It is to be observed that—(1) *cis*-terpin, when treated with hydrogen bromide, undergoes molecular change and yields the *trans*-dihydrobromide, whilst cineol, its anhydride, does not; and (2) that the molecular change takes place in the conversion of terpin into the dihydrobromide, whilst no molecular change occurs in the inverse production of terpin from the dihydrobromide. This apparently anomalous behaviour is probably to be explained by the intermediate formation of an unsaturated compound in those cases in which molecular change occurs.

A. H.

Chrysin. By S. v. KOSTANECKI (*Ber.*, 26, 2901–2305).—Chrysin, C₁₅H₁₀O₄, when boiled with alkali, yields phloroglucinol, benzoic and acetic acids, and also some acetophenone. It yields monalkyl ethers, which are insoluble in alkali. The monomethyl derivative is identical with tectochrysin.

A *diacetyl derivative*, C₁₅H₈O₄Ac₂, obtained by boiling it with acetic anhydride and anhydrous sodium acetate, crystallises in white needles, and melts at 185°.

The *sodium salt* of tectochrysin is obtained by adding sodium hydroxide to the alcoholic solution; it crystallises in intensely yellow needles, and is almost insoluble. *Acetylchrysin monomethyl ether*, OMe·C₁₅H₈O₃Ac, crystallises in white, lustrous needles, and melts at 149°.

The above reactions of chrysin are most easily explained by assigning to it the formula C₆H₂(OH)₂ < $\begin{array}{c} \text{O}-\text{C}^{\text{Ph}} \\ || \\ \text{CO}-\text{OH} \end{array}$ [OH : OH = 1 : 3].

E. C. R.

Dry Distillation of Jalapin. By E. KLIMENKO and Y. BANDALIN (*J. Russ. Chem. Soc.*, 25, 136–142).—Jalapin was distilled in portions

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of 20 grams from a small glass retort, at as low a heat as possible. The chief products obtained were—

1. An aqueous liquid boiling at 102–103°. This proved to be a solution of acetic acid of constant boiling point.

2. A brown liquid passing over between 170° and 220°, which, after treatment with sodium carbonate, and decomposition of the sodium salt with hydrochloric acid and extraction with ether, yielded tiglic acid.

3. A liquid collected above 220°, which partially solidified in the receiver. The solid, after purification, was found to be palmitic acid. J. W.

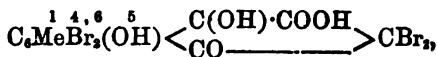
Constituents of Coto Bark. By O. HESSE (*Ber.*, 26, 2790–2795).—A continuation of the discussion with Ciamician and Silber. Mixtures of “methylprotocotoïn” (“oxyleucotin”), and “methylhydrocotoïn” (“benzoylhydrocoton”), or of “isomethylhydrocotoïn,” resemble “leucotin,” both in appearance and melting point (*Abstr.*, 1893, i, 417), but the melting point of leucotin is constant, whilst that of the mixture is not. The remainder of the paper deals with “paracotoïn,” “bromoparacotoïn,” “paracotoïnic acid,” “cotoïn,” and “dicotoïn.” A. R. L.

Colouring Matter of Cochineal. By W. V. MILLER and G. RONDE (*Ber.*, 26, 2647–2672).—Hlasiwetz and Grabowsky (*Annalen*, 141, 329) considered that De la Rue's carminic acid (*Annalen*, 64, 1) was a glucoside yielding on hydrolysis carmine-red and a sugar; the authors show, however, that this is incorrect, and that carminic acid is not altered in composition by boiling with dilute sulphuric acid. They have obtained 1·4 per cent. of tyrosine from cochineal extract, whereas de la Rue found only 0·4 per cent.

It has been pointed out by Will and Leymann (*Abstr.*, 1886, 252), that α - and β -bromocarmin yield methyl dibromohydroxyphthalic acid [$\text{Me} : \text{Br}_2 : \text{OH} : (\text{COOH})_2 = 1 : 4 : 6 : 5 : 2 : 3$] on oxidation. The authors find that the last-named acid is formed, together with bromoform, when α -bromocarmin is warmed with an excess of soda solution; they consider, therefore, α -bromocarmin to be an indone derivative of

the constitution $\text{C}_6\text{MeBr}_2(\text{OH}) \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CBr}_2$ (compare Zincke, *Abstr.*, 1888, 291, 1198).

Bearing in mind Zincke's observation, that indone derivatives are formed by the molecular degradation of halogenated derivatives of hydroxy- α -naphthaquinone, it seemed not improbable that β -bromocarmin, which contains in its molecule 1 atom of carbon less than α -bromocarmin, might belong to the latter class of compounds, especially as it bears a great resemblance to Diehl and Merz's bromhydroxynaphthaquinone (*Ber.*, 11, 1066). This hypothesis is borne out by the fact that β -bromocarmin is convertible into α -bromocarmin (see below). When β -bromocarmin (1 mol.) is dissolved in a solution of sodium carbonate (2 mols.) and treated in the cold with bromine (1 mol.), the hydroxy-acid,

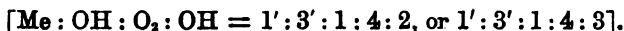


is formed. It crystallises with $3\text{H}_2\text{O}$, and melts at 106° or 208° , according as it is heated rapidly or slowly; if crystallised from ether, two melting points (somewhat higher) are also observed. When the hydroxy-acid is warmed with 50 per cent. acetic acid and bromine, it is converted into α -bromocarmin. These results show, therefore, that β -bromocarmin has the constitution represented by one of the formulæ $\text{CBr}=\text{CMe}\cdot\text{C}\cdot\text{CO}\cdot\text{C}\cdot\text{OH}$ or $\text{CBr}=\text{CMe}\cdot\text{C}\cdot\text{CO}\cdot\text{CBr}$
 $\text{C}(\text{OH})\cdot\text{CBr}\cdot\text{C}\cdot\text{CO}\cdot\text{CBr}$ or $\text{C}(\text{OH})\cdot\text{CBr}\cdot\text{C}\cdot\text{CO}\cdot\text{C}\cdot\text{OH}$.

If β -bromocarmin is dissolved in aqueous alkali, and the warm solution is treated with zinc-dust, it is converted into the *quinol*, $\text{C}_6\text{MeBr}_2(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{C}\cdot\text{OH}$
 $\text{C}(\text{OH})\cdot\text{CH}$, which crystallises in almost colourless needles, and darkens without melting when heated. The *tetracetyl* derivative, $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{O}_8$, melts at 206° . When the quinol is dissolved in alkali, and the solution is exposed to the air, a red salt separates; this, on treatment with acid, yields a substance which crystallises in yellow needles, melts at 263 – 265° , and resembles β -bromocarmin; when warmed with acetic acid and bromine, it is converted into α -bromocarmin.

The authors are unable to confirm Will and Leymann's observation (*loc. cit.*), that β -bromocarmin yields a colouring matter resembling carminic acid when treated with alkaline stannous chloride, and exposed to the air; the product is a yellowish-red compound, resembling the substance of melting point 263 – 265° mentioned above.

Carminic acid is, therefore, closely related to one of the two hydroxy-derivatives of methyl- α -naphthaquinone having the formulæ $\text{C}_{10}\text{H}_7\text{Me}(\text{OH})_2\text{O}_2$



The authors' analytical values for carminic acid and those of De la Rue agree well, but they are about 10 per cent. lower in carbon than those required for a compound of the above formula; compared with a dihydrate of such a compound, which might be the analogue of leuconic acid or triquinoyl (Nietzki and Benckiser), the agreement is better, but even then not satisfactory. It is pointed out, however, that carminic acid has, up to the present, only been obtained in an amorphous state. The authors find also that ruficoccin yields α -bromocarmin when treated with bromine in acetic acid solution; hence it must be nearly related to carminic acid, and they no longer accept Liebermann and van Dorp's statement (*loc. cit.*) that it is an anthracene derivative.

A. R. L.

Instability of Colouring Matters containing Carotene. By M. GERLACH (*Bied. Centr.*, 22, 786).—The fading of dyes containing carotene is not due to light, but to the oxygen of the air, as the change takes place in darkness as well as in light, but the colour is permanent in light when oxygen is excluded; at the same time the change is assisted by light.

E. W. P.

Conversion of Indoles into Quinolines. By A. FERRATINI (*Gazzetta*, 23, ii, 105—124).—This paper gives a detailed account of the work of which a short notice has already appeared (*Abstr.*, 1893, i, 602).

Action of Phenyl isocyanochloride on Derivatives of Phenylhydrazine. By M. FREUND and E. KÖNIG (*Ber.*, 26, 2869—2874).—Phenyl isocyanochloride, $\text{NPh}\cdot\text{CCl}_2$, is obtained by treating phenylthiocarbimide dissolved in chloroform with dry chlorine. It is a colourless oil, and boils at 205° .

Phenylphenylimido-oxybiazoline, $\text{N} \begin{smallmatrix} \text{CH}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{NPh}\cdot\text{C}\cdot\text{NPh} \end{smallmatrix}$, is obtained by heating dry formylphenylhydrazine with phenyl isocyanochloride. It crystallises in concentric, white needles, melts at 99° , and is not altered by boiling with water or soda solution. The *hydrochloride* crystallises in white needles, melts at $185\text{--}186^\circ$, and is decomposed by water.

Formylamidodiphenylcarbamide, $\text{NPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CHO}$, is obtained by heating moist formylphenylhydrazine with phenyl isocyanochloride. It crystallises in leaflets or needles, melts at 164° , is a feeble base, and is not altered by boiling with dilute alcoholic potash. It is also obtained by evaporating on the water bath, an alcoholic solution of the preceding oxybiazoline mixed with concentrated hydrochloric acid.

Phenylmethylphenylimido-oxybiazoline, $\text{N} \begin{smallmatrix} \text{CMe}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{NPh}\cdot\text{C}\cdot\text{NPh} \end{smallmatrix}$, is obtained from acetylphenylhydrazine in a similar way to the above oxybiazoline. It crystallises in white needles, melts at 75° , yields an oily hydrochloride, and, when boiled with alcoholic potash, yields a red solution which contains free phenylhydrazine. The *platinochloride* crystallises in tufts of shining needles, and melts at 92° .

Acetylamidodiphenylcarbamide, $\text{NPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{COMe}$, is obtained in a similar way to the above formyl compound. It crystallises from absolute alcohol in needles, melts at 181° , and is a weak base.

Phenylimidodiphenyloxybiazoline, $\text{N} \begin{smallmatrix} \text{CPh}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{NPh}\cdot\text{C}\cdot\text{NPh} \end{smallmatrix}$, is obtained by boiling benzoylphenylhydrazine with phenyl isocyanochloride and toluene. It crystallises in white needles, sinters at 102° , melts at 106° , and is insoluble in hydrochloric acid.

P-nylamidophenylimidophenylthiobiazoline, $\text{N} \begin{smallmatrix} \text{C}(\text{NHPh})\cdot\text{S} \\ \diagup \quad \diagdown \\ \text{NPh}\text{---}\text{C}\cdot\text{NPh} \end{smallmatrix}$, is obtained by warming diphenylthiosemicarbamide (m. p. 176°) with chloroform and phenyl isocyanochloride, and then decomposing with soda the hydrochloride thus obtained. It crystallises in white needles, and melts at 154° . The *hydrochloride* crystallises in pale yellowish-green, rhombic tablets, evolves hydrogen chloride at 140° , and then melts at 215° . The *nitroso-compound* is obtained in small, golden-yellow needles, melts at 110° , and is so unstable that it cannot be recrystallised.

Benzeneazophenylimidophenylthiobiazoline, $N \leftarrow \begin{smallmatrix} C(N:NPh) \cdot S \\ NPh \text{ — } C:NPh \end{smallmatrix}$, is obtained by warming phenylic isocyanochloride with a solution of diphenylthiocarbazon in chloroform. It crystallises in cherry-red needles, and melts at 180—181°. The *hydrazo-compound*, obtained by boiling it with a solution of ammonium sulphide in dilute alcohol, crystallises in white needles, and melts at 150°. E. C. R.

Derivatives of Oxybiazolone and Thiobiazolone. By E. KÖNIG (*Ber.*, 26, 2876; see also *Ber.*, 24, 1178).—*Orthotolylphenyl-oxybiazolone*, $C_7H_7 \cdot N \leftarrow \begin{smallmatrix} N \\ CO \cdot O \end{smallmatrix} > CPh$, crystallises from alcohol in needles, and melts at 120°.

Orthotolylphenyl-ψ-thiobiazolone, $C_7H_7 \cdot N \leftarrow \begin{smallmatrix} N \\ CS \cdot O \end{smallmatrix} > CPh$, crystallises from light petroleum in pale yellow prisms, and melts at 96°.

Orthotolylamido-oxybiazolone, $C_7H_7 \cdot N \leftarrow \begin{smallmatrix} N \\ CO \cdot O \end{smallmatrix} > C \cdot NH_2$, crystallises from a mixture of chloroform and light petroleum in interlacing needles, and melts at 131°.

Orthotolylamidothiobiazolone, $C_7H_7 \cdot N \leftarrow \begin{smallmatrix} N \\ CO \cdot S \end{smallmatrix} > C \cdot NH_2$, is obtained from orthotolylthiosemicarbazide (m. p. 156°) and carbonyl chloride. It crystallises in needles, and melts at 278—279°. E. C. R.

Triazole Derivatives. By M. FREUND and S. WISCHEWIANSKY (*Ber.*, 26, 2877—2881).—Thiocarbamides of the type



when treated with carbonyl chloride, lose 1 mol. of hydrogen sulphide, and are converted into bases of the triazole series having the constitution $NHR \cdot C \leftarrow \begin{smallmatrix} N-NH \\ NR \cdot CS \end{smallmatrix}$ or $NR \cdot C \leftarrow \begin{smallmatrix} NH \cdot N \\ NR \cdot C \cdot SH \end{smallmatrix}$.

Hydrazodicarbonthioamide, $NH_2 \cdot CS \cdot NH \cdot NH \cdot CS \cdot NH_2$, is obtained by boiling hydrazine sulphate with ammonium thiocyanate; it melts at 208°. When dissolved in toluene and heated with carbonyl chloride at 150—160°, it yields a yellow, insoluble compound which does not melt at 290°, and gave on analysis C, 23.11—22.65; H, 2.47—2.68; N, 36.93; and S, 26.8 per cent. Hydrazodicarbonthioamide, when treated with carbonyl chloride under the same conditions, is decomposed with the formation of ammonium chloride.

Hydrazodicarbonthioallylamide, $N_2H_2 \cdot (CS \cdot NH \cdot C_2H_5)_2$, is obtained by heating in a reflux apparatus hydrazine sulphate mixed with the theoretical quantity of sodium carbonate and a slight excess of allylthiocarbimide dissolved in alcohol. When heated with carbonyl chloride and toluene, hydrogen sulphide is eliminated, and a base of the composition $C_6H_{11}N_3S$ is formed. This base is also obtained by boiling the allylcarbamide with sodium carbonate or concentrated hydrochloric acid. It crystallises in interlacing needles, and melts at

147°. The *hydrochloride* crystallises with $3\text{H}_2\text{O}$, and melts at 49°. The *platinochloride* is obtained as a crystalline, sparingly soluble precipitate, and does not melt at 280°. The *nitroso-compound* crystallises in yellow leaflets, and melts at 105°. When the base is heated with methylic iodide and alcohol, it yields the methyl compound $\text{C}_6\text{H}_{11}\text{MeN}_4\text{S}\cdot\text{HI}$, which crystallises in leaflets, and melts at 167°. The *hydrochloride* of this last compound crystallises in leaflets, and does not yield a nitroso-derivative.

Hydrazodicarbonthiophenylamide, $\text{N}_2\text{H}_4\cdot(\text{CS}\cdot\text{NHPH})_2$, obtained in a similar way to the above allyl derivative, crystallises in white scales, and melts at 187°. When heated with carbonyl chloride, it yields the compound $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$, which melts at 239–240°.

E. C. R.

Formazyl Methyl Ketone. By E. BAMBERGER and P. DE GRUYTER (*Ber.*, 26, 2783–2786).—The compound of melting point 183°, obtained by the action of alcoholic ammonium sulphide on formazyl methyl ketone (*Abstr.*, 1892, i, 158), is *acetylamidrazone*,

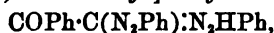


(compare this vol., i, 23). The *ureide*, $\text{N}_2\text{HPh}\cdot\text{CAc}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, prepared by treating it with potassium cyanate, melts at 183°. The *osazone*, $\text{N}_4\text{HPh}\cdot\text{CMe}\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{NH}_2$, obtained by treating *acetyl*-amidrazone or formazyl methyl ketone with phenylhydrazine, or boiling the former with dilute sulphuric acid, forms small, white needles, melts at 224°, and becomes reddish-violet on exposure to the air; concentrated sulphuric acid dissolves it with an intense bluish-violet coloration, whilst alkalis colour its alcoholic solution red. The *sulphate* melts at 211°; the *hydrochloride* melts at 114–115° apparently with dissociation. When the osazone is heated with glacial acetic acid at 180°, *phenylamidomethylsotriazole*, $\text{NPh}\left\langle \begin{smallmatrix} \text{N}\cdot\text{CMe} \\ \text{N}\cdot\text{C}\cdot\text{NH}_2 \end{smallmatrix} \right\rangle$, is formed; it is volatile with steam, and melts at 73°.

Acetylamidrazone yields an *acetyl* derivative, $\text{NHAc}\cdot\text{CAc}\cdot\text{N}\cdot\text{HPh}$, which forms yellowish-white, satiny needles, is insoluble in dilute mineral acids, melts at 143°, and, when heated with dilute acetic acid, is converted into *phenylacetylmethyltriazole*, $\text{NPh}\left\langle \begin{smallmatrix} \text{N}=\text{CAc} \\ \text{CMe}\cdot\text{N} \end{smallmatrix} \right\rangle$, melting at 88–89°. The latter gives a crystalline compound with sodium hydrogen sulphite, an *oxime* melting at 211–212°, and a *phenylhydrazone* which crystallises with 1 mol. of acetic acid, and melts at 128°, but loses the acetic acid, and becomes oily on exposure to the air.

A. R. L.

Formazyl Phenyl Ketone. By E. BAMBERGER and H. WITTE (*Ber.*, 26, 2786–2790).—*Formazyl phenyl ketone*,



is formed, together with a smaller amount of Claisen's phenylazo-benzoylacetone (*Abstr.*, 1888, 828), by the action of benzoylacetone or of benzoylacetic acid on diazobenzene in presence of free alkali; it crystallises in red, felted needles of a metallic lustre, and melts

at 141—142°. The *silver* salt explodes when heated, and the *acetyl* derivative, $\text{COPh}\cdot\text{C}(\text{N}_2\text{Ph})\cdot\text{N}_2\text{AcPh}$, melts at 154°.

a-Phenyltriazyl phenyl ketone, $\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{N}=\text{C}\cdot\text{COPh}$, is produced, together with aniline, by the action of concentrated mineral acids on formazyl phenyl ketone; it crystallises in golden-yellow bunches of needles, melts at 114°, and forms a hydrazone melting at 185°.

Benzoylamidrazone, $\text{COPh}\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{NH}_2$, is formed, together with aniline, when formazyl phenyl ketone is reduced with alcoholic ammonium sulphide; it melts at 152°, and gives Bülow's reaction. The *acetyl* derivative melts at 143—156°, according to the rapidity with which it is heated, and also gives Bülow's reaction. When heated, the *acetyl* derivative yields *methylphenylbenzoyltriazole*, $\text{NPh}\cdot\text{N}=\text{C}\cdot\text{COPh}$, which crystallises in colourless, silky needles, and melts at 55·5°.

A. R. L.

Isoquinine and Nichine. By E. LIPPMANN and F. FLEISSNER (*Monatsh.*, 14, 553—558; compare *Abstr.*, 1892, 81 and 83).—The authors confirm their previous statement (*loc. cit.*) as to the individuality of the base isoquinine, which melts at 185°, and which has been stated by Skraup (*Abstr.*, 1893, i, 56) to be a mixture of pseudoquinine and nichine.

Nichine may be obtained in largest yield by taking hydriodoquinine, recently precipitated in a crude form by ammonia, and adding to it silver nitrate, in slight excess above that required to completely precipitate the iodine; after removing the excess of silver with hydrochloric acid, the base is precipitated with ammonia. Nichine forms a well characterised hydrate, $3\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_2 + 2\text{H}_2\text{O}$, which crystallises in needles, and melts at 70°. The anhydrous base melts at 130—132°. Its acid solutions have a marked fluorescence, and give the characteristic quinine reaction with chlorine water and ammonia. The *dihydrochloride*, $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_2\cdot 2\text{HCl}$, forms small, granular crystals; the *acid sulphate* crystallises in long needles, and, like the *acid oxalate*, is very sparingly soluble in water and in alcohol.

G. T. M.

Relation between the Optical Rotary Power of Cinchonidine and its Salts: Influence of the Solvent on the Rotation. By C. A. SCHUSTER (*Monatsh.*, 14, 573—595).—Cinchonidine and its salts, including the hitherto unknown hydrobromide and hydriodide, are levorotatory. In alcoholic solution, all the salts, with the exception of the sulphate, show a maximum rotation, for like concentration, in 50 per cent. alcohol, and a minimum rotation in absolute alcohol. In the case of the sulphate, the maximum rotation is also given in a solution of 50 per cent. alcohol, but the minimum rotation is given by the aqueous solution. The difference in rotatory power of the various cinchonidine salts in aqueous solution is exceedingly small, and very closely resembles that calculated for the base, the maximum divergence

being obtained when the base is united with some weak acid, such as acetic acid. This behaviour is in harmony with the Arrhenius' dissociation theory. Comparisons of the rotatory powers of the compounds of cinchonidine with the halogen acids show that the rotation diminishes with increase in the molecular weight, according to Guye's rule.

G. T. M.

Alkaloids of the Root of *Corydalis cava*. By M. FREUND and W. JOSEPHI (*Annalen*, 277, 1—19; compare Abstr., 1892, 1366).—Corydaline, $C_{22}H_{27}NO_4$ (compare *loc. cit.*, also Dobbie and Lauder, *Trans.*, 1892, 244 and 605).—The specific rotatory power of the base in chloroform solution is $[\alpha]_D = +300.1$. The *hydrochloride* crystallises with $2H_2O$, and melts at $206-207^\circ$; and the *hydriodide* decomposes at 220° . When the methiodide is digested on the water bath with silver chloride and aqueous alkali, *methylcorydaline*, $C_{22}H_{29}NO_4$, is obtained; it crystallises from alcohol in colourless prisms, and melts at 112° ; the *hydrochloride* crystallises with $6H_2O$. *Methylcorydaline methiodide*, $C_{22}H_{29}NO_4MeI$, melts at $195-196^\circ$; both it and the methochloride are stable towards alkalis, thus recalling the similar indifference of the methohalogen compounds of hydrohydrastinine (Abstr., 1891, 1519), and the authors consider it probable that corydaline also contains a hydrogenised isoquinoline nucleus, having a methyl group united to the nitrogen atom.

Bulbocapnine.—The formula previously assigned by the authors to this base (*loc. cit.*) is incorrect; their present analyses agree with the formula $C_{18}H_{19}NO_4$. The base crystallises from alcohol in rhombic, hemihedral prisms, $a : b : c = 0.72700 : 1 : 0.73682$; its specific rotatory power in chloroform solution is $[\alpha]_D = +237.1$. The *hydrochloride*, *hydrobromide*, *hydriodide*, and *nitrate* are anhydrous, and decompose above 230° ; the *acid sulphate* has the formula $C_{18}H_{19}NO_4 \cdot H_2SO_4 + 2H_2O$; and the *methiodide* crystallises from water in lustrous needles, and melts at 257° . A determination by Zeisel's method indicated the presence of a single methoxy-group in bulbocapnine. Bearing in mind Dobbie and Lauder's observation that corydaline contains four methoxy-groups, the relation of the two bases is, perhaps, $C_{18}H_{19}N(OH)_3 \cdot OMe$ and $C_{18}H_{19}N(OMe)_4$.

Corycavine, $C_{23}H_{28}NO_5$ (see *loc. cit.*).

Corybulbine is the name given by the authors to a base isolated from commercial corydaline (*loc. cit.*); it differs from Dobbie and Lauder's corytuberine (*Trans.*, 1893, 485) in being insoluble in water. Lack of material precluded the determination of its formula. The authors leave the further development of the subject to Dobbie and Lauder.

A. R. L.

Organic Chemistry.

Dinitromethane. By P. DUDEN (*Ber.*, 26, 3003—3011).—*Dinitromethane*, $\text{CH}_2(\text{NO}_2)_2$, is obtained as potassium derivative by the action of dibromodinitromethane on arsenious anhydride, potash, and water at low temperatures; after remaining for some time, the reaction is completed by heating in a reflux apparatus; the product is then suspended in water and ether and decomposed by dilute sulphuric acid; on evaporating the ethereal solution at a low temperature, the dinitro-compound remains as a yellow oil, having a characteristic acid odour. It rapidly decomposes at ordinary temperatures, even in a sealed tube, and does not solidify at -15° ; in ethereal or benzene solution, it is stable, and is volatile with benzene vapour, and also with steam. By the action of bromine water on dinitromethane, the dibromo-derivative is regenerated; with hydroxides, carbonates, sulphites, and nitrites, metallic derivatives are formed, carbonic anhydride, sulphurous anhydride, and nitrous acid being liberated. The *potassium* derivative, $\text{CH}(\text{NO}_2)_2\text{K}$, crystallises from water in pale yellow, monoclinic crystals; the aqueous solution is neutral; by the action of concentrated or dilute acids at ordinary temperatures, decomposition takes place, with evolution of nitrous fumes; on heating it to about 205° , potassium carbonate, water, carbonic anhydride, nitric oxide, and nitrogen are formed. Villiers' statement that it is unstable is incorrect; when pure, it undergoes no change on exposure to air; in a closed vessel, a slight, superficial decomposition takes place. The *ammonium* derivative crystallises from alcohol-ether in slender, pale yellow needles, which explode at about 105° . The *phenylhydrazine* compound forms intensely yellow needles, and melts at 101° with decomposition. The *copper* derivative is pale green, and readily decomposes in aqueous solution. The *barium* derivative, $(\text{CHN}_2\text{O})_2\text{Ba} + 2\text{H}_2\text{O}$, crystallises in pale yellow needles; on heating, it becomes anhydrous and darkens, and finally explodes. The *silver* derivative, $\text{CH}(\text{NO}_2)_2\text{Ag}$, crystallises in lustrous, yellowish-green plates, and decomposes rapidly on exposure to light, on boiling with water, or on heating to 135° . Dinitroethane and dinitropropane are formed by the action of methylic iodide and ethylic iodide respectively on the silver derivative at ordinary temperatures. By the action of nitrous acid on potassium dinitromethane, *isonitrosodinitromethane*, $\text{NOH}\cdot\text{C}(\text{NO}_2)_2$, appears to be formed; it is extremely unstable, dissolves in ether with a blood-red colour, and forms a sodium and a silver derivative, neither of which could be completely freed from nitrite. Ammonia is eliminated by the reduction of dinitromethane in acid solution, but, on treatment with sodium amalgam at 0° , methylazaurolic acid, $\text{CH}_2\text{N}_2\text{O}$, is formed. Potassium dinitromethane and diazobenzene hydrochloride in glacial acetic acid solution yield a compound which has the formula $\text{C}(\text{NO}_2)_2(\text{NP}_2\text{h})_2$, and crystallises in orange-red needles, melting at 75° with decomposition; it is readily soluble, and decomposes on boiling, or by the action of alkalis.

J. B. T.

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Synthesis of Nitroparaffins. By I. BEVAD (*J. pr. Chem.*, [2], 48, 345—383; compare Abstr., 1893, i, 242, 382).—The zinc alkylides react with the halogen nitro-derivatives of the hydrocarbons displacing the halogen atom (1) by an alkyl group, (2) by hydrogen, and (3) by both alkyl group and hydrogen. The first reaction produces secondary and tertiary nitro-compounds more complex than those treated (see Abstr., 1893, i, 242); the second results in the formation of the same primary or secondary nitro-compound, whose halogen derivative was treated; whilst the third only occurs with those compounds which contain not fewer than 2 halogen atoms, and produces primary and secondary nitro-compounds more complex than those treated.

A. G. B.

Action of Reducing Agents on Potassium Nickelocyanide. By T. MOORE (*Chem. News*, 68, 295).—The author has investigated the nature of the red coloration produced when a strip of zinc is immersed in a solution of potassium nickelocyanide containing ammonium chloride and ammonia; the colour is very fugitive, and oxygen and zinc compounds aid its destruction. By treating the nickelocyanide with sodium amalgam in an atmosphere of hydrogen, a deep red solution is readily obtained, which gives, amongst others, the following reactions:—With silver nitrate, a heavy, black precipitate of metallic silver; with mercuric chloride, a grey precipitate; with lead acetate, a black precipitate, insoluble in potassium hydroxide or acetic acid, decomposed on drying, leaving yellow lead oxide; with bismuth nitrate, a black precipitate; with arsenious anhydride, a deep brown precipitate; gold chloride is slowly reduced. The solution is, moreover, decolorised by permanganate, dichromate, hydrogen peroxide, &c. When acidified, it yields an orange-yellow, flocculent precipitate, which, after filtration and washing with cold water, dissolves in alkalis to a red solution; the precipitate darkens and becomes dirty blue in the air, and decomposes completely on drying, even in hydrogen, yielding apparently a mixture of nickel oxide and cyanide. The instability of the substance has, so far, prevented its being submitted to analysis, but experiments indicate that the red solution absorbs 2 atoms of oxygen for every 3 atoms of nickel present.

D. A. L.

Oxidation of Potassium Cobaltocyanide. By T. MOORE (*Chem. News*, 68, 295—296).—The equation $2K_4COCy_6 + 2H_2O + O = K_4C_2O_2Cy_{12} + 2KHO + H_2O$ has been regarded as representing the conversion of potassium cobaltocyanide into the cobalticyanide in the presence of free hydrocyanic acid and with access of air. On adding a mixture of sodium hydroxide and potassium cyanide to a solution of cobalt and agitating with air until absorption ceases, the author finds that the liquid becomes deep red-brown, and that oxygen is taken up in quantities varying between 8000 to 9600 c.c. per 59 grams of cobalt, instead of 5600 c.c. as required by theory. In similar experiments, with the sodium hydroxide omitted and the liquid strongly acidified instead, the solution became yellow, and oxygen was absorbed to the extent of 7450 to 7516 c.c. per 59 grams of cobalt. As no by-products were observed, and as these oxidised solutions evolve oxygen

on boiling, it is suggested that there are higher cobalticyanides than the one indicated above.

D. A. L.

Rate of Etherification of Hydrogen Fluoride. By M. MESLANS (*Compt. rend.*, 117, 853—856).—The action of hydrogen fluoride on alcohol at about 200° (Abstr., 1893, i, 186) is at first rapid, but after four hours becomes slower, and attains its maximum in 10 hours. The temperature exerts great influence on the rate of change; at 170° the velocity of etherification is 10 times as great, and at 190° it is 20 times as great, as at 140°.

When the alcohol is in excess, no methylic fluoride is formed, and the sole product is ordinary ether. An excess of hydrogen fluoride, on the other hand, greatly accelerates the change, and the velocity of etherification is 60 times as great with a mixture of 4 mols. of the acid and 1 mol. of alcohol as it is with a mixture in equivalent proportions.

Thermal disturbances indicate the existence of stable alcoholates of hydrogen fluoride, and it would seem that when the alcohol is in excess, a part combines with the hydrogen fluoride to form stable alcoholates, whilst the remainder acts on the ethylic fluoride that is formed, and produces ordinary ether, whereas, when the hydrogen fluoride is in sufficient excess, no alcohol remains uncombined, and the secondary reaction does not take place. No ether is formed when 4 mols. of the acid are mixed with 1 mol. of alcohol, and with lower proportions of the acid the apparent velocity of etherification is the difference between the real velocity and the velocity of the secondary reaction.

The presence of water greatly reduces the rate of etherification, but some change takes place at 220°, even when 2 mols. of water are present for each mol. of hydrogen fluoride.

C. H. B.

Electrolytic Oxidation of Glycerol. By W. E. STONE and H. N. MCCOY (*Amer. Chem. J.*, 15, 656—660).—A current of less than 0.3 ampère from one or two dichromate cells was passed between platinum electrodes placed in 10 per cent. aqueous glycerol, in which various inorganic substances were dissolved to lessen the resistance.

With dilute sulphuric acid or sodium nitrate (0.1 per cent.), the temperature rose, and the liquid, which in the latter case soon became acid, acquired the power of reducing alkaline copper tartrate in the cold, and yielded the rosaniline reaction for aldehydes; glycerose-aldehyde was, therefore, probably formed, and subsequently polymerised into glycerose. In the first case, an odour of acraldehyde was ultimately noticeable.

With a small quantity of sodium hydroxide, a yellow or yellowish-brown colour was first produced, probably due to the presence of a hexose, and after some hours the solution became acid in reaction; the acid in one case corresponding with as much as 80 per cent. of that theoretically producible from the glycerol. The solution reduced alkaline copper tartrate in the cold, and further, on boiling, showing the presence of a hexose. No odour of acraldehyde was perceptible.

When the alkalinity of the solution was maintained, and the

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current passed for several days, the power of reducing alkaline copper tartrate in the cold was at length lost, although, on boiling, a much more powerful reduction was obtained. The presence of a hexose was confirmed by the preparation of its osazone, which melted at 200° (m. p. d-glucosazone, $204-205^{\circ}$), and by its resolution into carbonic anhydride by fermentation with yeast.

An unsuccessful attempt was made to prepare the optically active modification of glyceric acid from one and the same portion of the inactive acid. JN. W.

Acetyl and Benzoyl Derivatives of Pentoses. By W. E. STONE (*Amer. Chem. J.*, **15**, 653—656).—*Tetracetylxylose*, $C_8H_8O_8Ac_4$, is prepared by heating xylose with acetic anhydride and fused sodium acetate. It crystallises in fine needles, melts without decomposition at $123.5-124.5^{\circ}$, and has a bitter taste. The specific rotatory power in anhydrous alcoholic solution is $[\alpha]_D = -25.43^{\circ}$, without multirotation. It is resolved by acid hydrolysis into its proximate constituents.

Tetracetylabinose is prepared in a similar manner. It forms a thick syrup which solidifies when immersed in a mixture of solid carbonic anhydride and ether, and afterwards melts at -7.6° . The specific rotatory power in anhydrous alcoholic solution is $[\alpha]_D = +26.39^{\circ}$. Its taste and its behaviour towards acid hydrolytic agents resemble that of its isomeride.

Attempts to prepare the corresponding benzoyl derivatives yielded crystalline substances having constant melting points ($164-165^{\circ}$ and $68-69^{\circ}$), but compositions agreeing with those of no single derivative; they are probably mixtures. JN. W.

Constitution of Glucose and the Glucosides. By L. MARCH-LEWSKI (*Ber.*, **26**, 2928—2930).—The author has previously shown (*Trans.*, 1893, 1137) that the constitution of the glucosides may readily be explained by the help of 'Tollens' or other similar formula for glucose; no evidence was, however, adduced to show with which carbon atoms the oxygen atom present in the "ethylene oxide" form is combined. Inasmuch as the glucosides do not behave as aldehydes under any conditions, it is probable that the residue combined with the glucose is united with the carbon atom from which the aldehyde group of the original glucose is produced; and, further, as a second phenylhydrazine residue may be combined with the carbon atom next to the aldehyde group in glucose, but not in the glucosides, it seems probable that the atom complex of this carbon atom has also undergone alteration. From this, the author concludes that the constitution of the glucosides is represented by the formula $O < \begin{array}{c} CH \cdot [CH \cdot OH]_3 \cdot CH_2 \cdot OH \\ | \\ CH \cdot OR \end{array}$.

As evidence against the supposition that the radicle displaces the hydrogen of one of the alcohol groups, the author adduces the fact that an aqueous solution of sodium glucosate is totally unaffected by phenylhydrazine. H. G. C.

The Sugar of Phlorizin. By O. HESSE (*Annalen*, **277**, 302—304).—The author defends his remarks (*Annalen*, **172**, 356) that the

sugar (phlorose) from phlorizin is distinct from glucose (dextrose), despite the observations of Rennie (*Trans.*, 1887, 634), Fischer (*Abstr.*, 1888, 590), and Schunk and Marchlewski (*Abstr.*, 1893, i, 384). On extracting, with methylic alcohol, the sample of sugar which was originally faintly-yellowish but which after 15 years had become brown, glucose was obtained from the extract. Even this fails to convince the author that the original sugar is identical with glucose; he admits merely that phlorose is capable of being converted into glucose, but whether or not the change is brought about by the agency of lower organisms cannot be said.

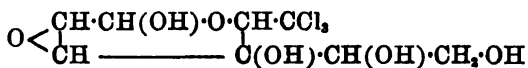
A. R. L.

Chloralose. By M. HANRIOT and C. RICHET (*Compt. rend.*, 117, 734—737).—Chloralose (*Abstr.*, 1893, i, 247) melts at 187°, and dissolves in alcohol, but is only slightly soluble in water or ether. Its boiling aqueous solution reduces neither ammoniacal silver nitrate nor Fehling's solution. Acids are without effect on it, but alkalis change the colour of the hot solution to brown. Chloralose is not affected by nascent hydrogen from sodium amalgam. With acids and acid chlorides, it yields di- and tetra-substitution derivatives, *tetracetylchloralose*, melting at 145°, and *tetrabenzoylchloralose* crystallising in prisms melting at 138°. Oxidation converts chloralose, with evolution of carbonic anhydride, into *chloralic acid*, $C_7H_5Cl_3O_6$, which crystallises in anhydrous needles melting at 212°, soluble in alcohol or ether, but only slightly soluble in water.

All these derivatives of chloralose are without physiological activity.

Parachloralose (*loc. cit.*) is insoluble in most reagents, melts at 227°, and sublimes if heated slowly. Like chloralose, it is not affected by hydroxylamine, phenylhydrazine, or dilute acids, but it is very slowly attacked by boiling solutions of alkalis. With acids and acid chlorides, it yields di- and tetra-derivatives; *tetracetylparachloralose* crystallises in long needles melting at 106°, and boiling at about 250° under a pressure of 25 mm. When oxidised, parachloralose yields carbonic anhydride and *parachloralic acid*, which crystallises with $2H_2O$ in efflorescent tables melting at 202°, and very soluble in alcohol or ether, but only slightly so in cold water.

These properties indicate that neither chloralose nor parachloralose have the aldehyde functions of glucose and chloral. They cannot be regarded as ethereal salts of glucose, and it would seem that they have the following constitution.



and $O < \begin{array}{c} \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{C}(\text{OH}) \cdot \text{CCl}_3 \\ \text{CH} \text{ ————— } \text{C}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH} \end{array}$, although the position of the anhydric oxygen is somewhat uncertain. C. H. B.

Decomposition Products of Calcium Sucrate. By E. O. v. LIPPMANN (*Ber.*, 26, 3057—3059).—A sample of calcium sucrate which had been preserved for five years was found to contain no

sugar; the lime was combined with carbonic, formic, acetic, and oxalic acids. Another sample of calcium succate, which had been preserved for two years, was treated with boric acid suspended in alcohol; the alcoholic solution yielded an acid syrup from which crystals were obtained, and identified by the author as acetonedicarboxylic acid (m. p. 136°).

E. C. R.

Decomposition Products of Cane Sugar. By E. O. v. LIPPMANN (*Ber.*, 26, 3059—3061).—During the preparation of sugar-candy from pure white crystallised sugar, the mass sometimes becomes faintly acid, owing to the formation of decomposition products. An examination of the product showed the presence of a small quantity of a fruity ether and a dimethylfurfuran, $C_8H_{10}O$, which melts at 94° . Trihydroxybutyric acid and a small quantity of trihydroxyglutaric acid, $C_6H_8O_8$, were separated. The latter melts at 125° , and is dextro-rotatory, $\alpha_D^{20} = 20.8^{\circ}$. A syrupy acid was also obtained, which is probably identical with the hexepinic acid described by Maumené, and, finally, small quantities of catechol and protocatechuic acid.

E. C. R.

Carbohydrates Soluble in Water obtained from Malt and Barley. By G. DÜLL (*Chem. Zeit.*, 17, 67—68 and 100).—Jalowetz came to the conclusion that the optical and reducing properties of cold water malt extract are to be attributed to the presence of dextrin and glucose (dextrose). The author extracts malt meal with boiling 80 per cent. alcohol for five hours, distils off the alcohol, takes up the residual syrup with water, and dialyses the solution. The grains, after being boiled with 80 per cent. alcohol, are extracted with cold water, and the solution submitted to dialysis. In this way it is shown by the optical rotation, the copper test, and the phenylhydrazine reaction, that the carbohydrates saccharose and invert sugar are present along with a gum (galactoxylan, and perhaps other gums), and besides these there are inorganic matter, proteids, fat, choline, &c. (compare also Kühnemann, *Ber.*, 8, 202 and 307; Kjeldahl, *Zeit. ges. Brauw.*, [2], 4, 447). This applies both to air-dried and kiln-dried malt. There is no doubt that kiln-dried malt contains ready-formed invert sugar, and the author shows that the same is true of green malt, for when the latter is extracted with 0.2 per cent. ammonia, which arrests the action of the saccharose-hydrolysing enzyme, the presence of which Kjeldahl has recognised, the solution contains invert sugar.

Experiments with barley showed that it contained a non-reducing sugar yielding phenylglucosazone; the author therefore concludes that the only soluble carbohydrate present in barley besides the gum is saccharose. The aqueous extracts of barley generally gave the choline reaction.

A. R. L.

Note.—The author makes no reference to the well-known experiments of O'Sullivan on the sugars of cereals and germinated grain. It is especially surprising that the author fails to notice the fact that O'Sullivan has conclusively proved the presence of raffinose in barley (*Trans.*, 1886, 70). It is quite conceivable that the presence of

raffinose might escape detection by the osazone test, or it may be that raffinose is not an invariable constituent of barley.

A. R. L.

Starch. By C. SCHEIBLER and H. MITTELMEIER (*Ber.*, **26**, 2930—2937).—In this paper, the authors reply to the recent communication of Lintner and Düll on the same subject (this vol., i, 5), pointing out that the results there detailed have, in some cases, already been described by the authors (*Abstr.*, 1891, 33). They further do not agree with the theory proposed by Lintner and Düll, and devote the chief portion of the paper to an extension of their own theory as to the constitution of starch and the dextrins.

According to this there is no difference in principle between the constitution of starch and the dextrins, and that of the biose such as cane sugar and maltose, and of the trioses such as melitriose, the dextrins and starch simply containing a much larger number of glucose residues in the molecule. The combination between two glucose molecules to form a biose may take place in two ways, according as either one or both of the carbonyl groups take part in the combination; in the former case, the compound formed has still the properties of an aldehyde, but not in the latter; this is exemplified in the cases of maltose and cane sugar. The former method of combination the authors term the monocarbonyl linking, and the latter the dicarbonyl linking.

In the case of starch, the glucose residues are all combined by dicarbonyl linkings, and do not therefore reduce Fehling's solution or react with phenylhydrazine. When treated with acids or ferments such as diastase, the first action is the hydrolysis of the starch molecule at one of the dicarbonyl linkings, yielding two molecules, each of which contains an aldehyde group, that particular glucose residue being connected with the remainder of the molecule by a monocarbonyl linking. These new substances form the dextrins, and as the hydrolysis of the starch molecule probably takes place simultaneously at several of the dicarbonyl linkings, a number of dextrins are simultaneously formed; by the further action of the ferment on these, however, they are split up into dextrins of smaller molecular weight, and, finally, when invertase is employed, into maltose; with acids, however, the hydrolysis goes further, and the whole is converted into glucose. The process is in fact similar to that observed in the case of melitriose, which is resolved first into melibiose and fructose, the former being in turn resolved into glucose and galactose (*Abstr.*, 1890, 226, 1085).

H. G. C.

Crystallisation of Cellulose. By E. GILSON (*Chem. Centr.*, 1893, ii, 530).—Under the term "cellulose," the author includes the carbohydrates of the membrane which are insoluble in dilute acids or alkalis, but soluble in sulphuric acid, and which are coloured blue by iodine in presence of concentrated sulphuric or phosphoric acid.

The author finds that if sections of cellular tissue are allowed to remain for a time in contact with Schweizer's reagent, then washed carefully first with ammonia and then with water, so that the copper compound dissolves gradually and the cellulose is precipitated slowly,

the latter is found in the interior of the cells in the form of nodular or arborescent crystals. These are insoluble in dilute acids and alkalis, but soluble in concentrated sulphuric acid, and show also the other characteristics of cellulose. To obtain the crystals certain precautions are necessary, one of these being the complete removal of starch before treating the section with Schweizer's reagent. The reaction has been successfully carried out with a large number of phanerogams and cryptogams. Objects such as the seed grains of *Coffea arabica*, *Phytelephas macrocarpa*, and *Strychnos nux vomica*, which contain reserve cellulose, show plainly the presence of two different substances in the membrane, one of which is coloured blue by iodine and zinc chloride, and can be obtained crystalline in the above manner; the other is amorphous and gives no coloration with iodine. Cotton-wool, wood, and tunicin may likewise be partially converted into crystals.

The author concludes that all membranes which are coloured by ammonia and zinc chloride can be in part obtained crystalline by the above treatment, and that only the portion which is thus coloured can be crystallised. The crystalline product has always the same appearance and properties, and appears therefore to be a distinct compound. All membranes contain cellulose, together with a considerable amount of other substances which are not coloured by the above reagent; whilst reserve cellulose consists of a mixture of the crystallisable cellulose with other carbohydrates. As the cellulose always crystallises on the interior of the cells, it must occupy the inner portion of the membrane, and when dissolved in Schweizer's reagent it diffuses very little, if at all, through the membrane. This observation affords an explanation of the fact that cellulose cannot be completely dissolved by Schweizer's reagent, and also of the manner in which Frey was led to believe in the existence of a metacellulose, which is only soluble in the reagent after treatment with acids, for the acid dissolves or attacks the other constituents of the membrane, and allows the reagent free access to the cellulose hitherto held in the interior of the cells.

To obtain the cellulose in larger crystals, a solution of the pure substance in ammoniacal copper oxide is allowed to remain in a loosely-closed vessel; the ammonia slowly escapes, and cellulose and copper oxide are precipitated. The latter is removed by washing with hydrochloric acid and water, when the cellulose remains in nodular crystals; on treatment with acids, it yields glucose as the sole product of hydrolysis. The mannosocellulose of Schulze is a mixture of cellulose with another carbohydrate for which the author proposes the term *paramanan*; this may also be obtained in the form of nodular crystals.

The membrane of all vegetable cells with the exception of the fungi appears to contain cellulose, which occurs in the free state. In the case of woody membranes, however, it is probably in combination with another hydrocarbon or allied compound. H. G. C.

Oxidation of Aliphatic Aldehydes and Ketones by Nitric acid. By R. BEREND and J. SCHMITZ (*Annalen*, 277, 310—339).—

This paper commences with a bibliographical *résumé* of the subject. A preliminary account of the experiments on the action of nitric acid on acetone has already been published (compare Abstr., 1893, i, 303). The yellow oil thus obtained is decomposed when boiled with water yielding nitrous oxide, carbonic anhydride, formic, acetic, and oxalic acids, and hydrogen cyanide. Chloromethylglyoxime, obtained by warming chlorisonitrosoacetone with hydroxylamine hydrochloride (*loc. cit.*), melts with decomposition at 182—183°. Nitrosoxymethylglyoxime, $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NOH})\text{O}\cdot\text{NO}$ (*loc. cit.*), obtained by treating an aqueous solution of the yellow unstable oil with hydroxylamine hydrochloride, when oxidised with nitric acid of sp. gr. 1.37 saturated with nitrous acid, gives a compound $\text{C}_3\text{H}_5\text{N}_3\text{O}_4$, which crystallises from aqueous alcohol in colourless, brittle plates, and melts at 66—67°; when heated with alcoholic potash, it dissolves, forming a yellow solution having the odour of peppermint. Its constitution is probably $\begin{array}{c} \text{CMe}\cdot\text{C}\cdot\text{NO}_2 \\ \parallel \qquad \parallel \\ \text{NO}\cdot\text{ON} \end{array}$, that is, it belongs to the class of oxime peroxides first prepared by Koreff (Abstr., 1886, 363), and subsequently studied by Hollemann (Abstr., 1888, 275; 1889, 49) and by Angeli (Abstr., 1891, 890; 1892, 1198; 1893, i, 310, 355). The compound of melting point 188—191°, obtained by treating nitrosoxymethylglyoxime with a solution of sodium hydrogen carbonate, is shown, by the cryoscopic method, to have a molecular weight corresponding with the formula $\text{C}_3\text{H}_5\text{N}_4\text{O}_4$. If this is treated with nitric acid saturated with nitrous acid, a compound $\text{C}_3\text{H}_5\text{N}_5\text{O}_5$ is obtained, which melts at 113.5—115°.

When paraldehyde is oxidised with nitric acid according to De Forcrand's directions (*Bull. Soc. Chim.*, [2], 41, 242), and the product is distilled under diminished pressure until its volume is reduced to one-fourth, formic and acetic acids, together with unaltered paraldehyde and a small quantity of formaldehyde, pass over, whilst on distilling the residue at the ordinary pressure glyoxal passes over.

In conclusion, the authors confirm Ljubavin's observation that the production of glyoxaline from ammonia and glyoxal depends on the initial formation of formaldehyde, which condenses with the ammonia and glyoxal. In the preparation of glyoxaline from glyoxal and ammonia, it is therefore advisable to add formaldehyde.

A. R. L.

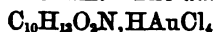
Derivatives of Acetylacetone. By C. U. ZANETTI (*Gazzetta*, 23, ii, 299—312).—Knorr (Abstr., 1887, 275) obtained 3:5:2:4-dimethyldiacetylpyrroline by reducing a mixture of ethylic nitrosoacetate and ethylic acetoacetate. The author obtains the same pyrroline derivative by reducing with zinc dust the product of the action of potassium nitrite (1 mol.) on acetylacetone (2 mols.) in acetic acid solution; its *aurochloride*, $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}\cdot\text{HAuCl}_4$, crystallises in small, yellow needles, which begin to decompose at 70° and melt at 120—130°.

3:5:2:4-Dimethyldiacinnamylpyrroline, $\text{C}_{24}\text{H}_{27}\text{O}_2\text{N}$, is obtained by the action of benzaldehyde on the above diacetyl derivative in alkaline solution; it forms small needles melting at 215—216°.

Nitrosoacetylacetone, $\text{C}_6\text{H}_7\text{NO}_3$, is an intermediate product in the formation of dimethyldiacetylpyrroline, and is isolated by dissolving acetylacetone in the minimum quantity of 12 per cent. potash, cooling with ice, adding the calculated quantity of potassium nitrite, and then, gradually, a slight excess of dilute sulphuric acid. Ether extracts the nitroso-derivative from the solution; it is ultimately obtained in pearly, flattened needles, or scales, which melt at 75° . It is very soluble in water, alcohol, or ethylic acetate, but only sparingly in benzene or light petroleum. It has a marked, although somewhat transient, antipyretic action on the animal system, and toxic symptoms are observed on administering a dose of 0.2 gram per kilo. of body weight. With hydroxylamine, it yields a product which seems to be a mixture. On reducing nitrosoacetylacetone with zinc dust in acetic acid solution in the cold, *dimethyldiacetaldine*, (?) $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_2$, is obtained; it forms yellow needles melting at $101\text{--}102^\circ$, and acts as a feeble base. If the reduction proceeds at a high temperature, a liquid product is obtained which gives an unstable *platinochloride*; the author proposes to examine these reactions later.

Symmetrical tetracetylene (compare Harrow, *Annalen*, 201, 144) may be prepared by adding an ethereal solution of iodine to an ethereal solution of sodioacetylacetone, filtering, removing the sodium iodide by treatment with water, and crystallising the residue from acetic acid. On boiling tetracetylene with concentrated hydrochloric acid, it yields *dimethyldiacetylfurfuran*, $\begin{matrix} \text{C}_6\text{H}_6\text{O}_2 \\ \text{C}_6\text{H}_6\text{O}_2 \end{matrix} \begin{matrix} \text{C}_6\text{H}_6\text{O}_2 \\ \text{C}_6\text{H}_6\text{O}_2 \end{matrix} > \text{O}$; this crystallises in long, waxy needles melting at 62.5° .

3:4:2:5-Dimethyldiacetylpyrroline, $\begin{matrix} \text{C}_6\text{H}_6\text{O}_2 \\ \text{C}_6\text{H}_6\text{O}_2 \end{matrix} > \text{N}$, is prepared by boiling tetracetylene with ammonium acetate and acetic acid; it separates on the addition of alkali, and crystallises from hot water in opaque, white needles melting at $180\text{--}181^\circ$. It is readily soluble in alcohol or boiling water, but only sparingly in ether or ethylic acetate. It behaves as a feeble base, yielding a *hydrochloride* which crystallises in white needles; this is decomposed by water and gives off hydrogen chloride in a vacuum. The *aurochloride*,



crystallises in yellow needles, and begins to decompose at 100° . A list of reactions of the base is given. A crystalline *hydrobromide* separates from the solution of the base in fuming hydrobromic acid; on adding bromine to the solution, however, an unstable *perbromide*, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}, \text{HBr}, \text{Br}_2$, separates as a reddish mass, which yields the pyrroline when treated with sodium carbonate.

3:5:2-Dimethylacetylpyrroline is soluble in concentrated hydrochloric acid, and yields a fairly stable, yellow, crystalline *aurochloride*, $\text{C}_8\text{H}_8\text{ON}, \text{HAuCl}_4$. 2-Acetylhomopyrroline is moderately soluble in hydrochloric acid; its *aurochloride* forms minute needles and is less stable than the preceding one. 2:5-Diacetylpyrroline is very sparingly soluble in hydrochloric acid, and yields an *aurochloride* which is decomposed by water.

On treating a hot alkaline solution of acetylacetone with hydrazine

sulphate, 3:5-dimethylpyrazole is deposited. Acetylacetone reacts with benzaldehyde, giving a mixture of several cinnamyl derivatives; it is perhaps possible to separate these by taking advantage of their behaviour towards phenylhydrazine.

W. J. P.

Condensation of β -Diketones with Carbamide, Guanidine, and Thiocarbamide. By P. N. EVANS (*J. pr. Chem.*, 45, 489—517).

—*Acetylacetonecarbamide*, $\text{CO} < \begin{smallmatrix} \text{N:CMe} \\ \text{N:CMe} \end{smallmatrix} > \text{CH}_2$, is obtained, as a salt, by the condensation of acetylacetone and carbamide (equal molecules) with sulphuric or hydrochloric acid. The *hydrochloride* crystallises in rectangular plates, and does not yield ammonia when boiled with concentrated sodium hydroxide. It gives no precipitate with platinic chloride. When treated with diazobenzene chloride and sodium acetate, it gives an orange, crystalline precipitate which quickly turns dark red; this compound is a powerful dye. The *sulphate*, $\text{C}_6\text{H}_8\text{N}_2\text{O}_4\text{H}_2\text{SO}_4$, forms thick, transparent crystals, and melts at 209° . Acetylacetonecarbamide is most easily obtained by treating the sulphate with barium carbonate, evaporating the filtrate to dryness, and extracting with benzene. It crystallises from water in short, thick prisms, melts at 198° , and has both basic and weak acid properties. It is not altered by treatment with nitrous oxide or acetic chloride. The *silver salt*, $\text{C}_6\text{H}_8\text{N}_2\text{OAg}$, was obtained; the *mercury salt*, $\text{C}_6\text{H}_8\text{N}_2\text{OHg}$, is a yellow precipitate. On bromination, a *derivative*, $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{Br}_2$ ($= \text{CO} < \begin{smallmatrix} \text{NBr-CMe(OH)} \\ \text{NBr-CMe(OH)} \end{smallmatrix} > \text{CH}_2$), is obtained; it crystallises in white, flocculent crystals, turns grey at 90° , blackens at $143\text{--}145^\circ$, and dissolves in ammonia.

Diurimidiacetylacetone, $\text{CH}_2(\text{CMe:N}\cdot\text{CO}\cdot\text{NH}_2)_2$, is obtained by the condensation of acetylacetone with 2 mols. of carbamide. The *hydrochloride*, $\text{C}_7\text{H}_{12}\text{N}_4\text{O}_2\cdot\text{HCl}$, crystallises in slender, colourless needles, melts at 180° , does not give a precipitate with platinic chloride, and easily yields ammonia when heated with potassium hydroxide. When heated with silver oxide, it yields carbamide and acetylacetonecarbamide. A molecular compound of the sulphates of diurimidoacetylacetone and carbamide, $\text{C}_7\text{H}_{12}\text{N}_4\text{O}_2\cdot\text{CH}_4\text{H}_2\text{O}_4\cdot\text{H}_2\text{SO}_4$, crystallises in aggregates of slender needles, and melts at 142° . Diurimidoacetylacetone, prepared by treating this sulphate with barium carbonate, melts at 199° , and is identical with the compound obtained by A and C. Combes (*Bull. Soc. Chim.*, [2], 7, 791) from acetylacetone and carbamide.

The condensation products of acetylacetone with thiocarbamide are obtained in a similar way to those with carbamide.

Acetylacetone-thiocarbamide, $\text{CS} < \begin{smallmatrix} \text{N:CMe} \\ \text{N:CMe} \end{smallmatrix} > \text{CH}_2$, crystallises in yellow needles, melts at 210° , and easily yields compounds with metallic salts. The *silver salt*, $\text{C}_6\text{H}_7\text{N}_2\text{SAg}\cdot\text{AgNO}_3$, is obtained as a white precipitate on adding silver nitrate to the aqueous solution. The aqueous solution also gives a white precipitate with mercuric chloride, a yellow precipitate with platinic chloride, an orange color-

tion and then a yellowish precipitate with ferric chloride, and a dirty white precipitate with copper acetate. The *hydrochloride*,



crystallises in slender, yellow needles, and volatilises when heated on platinum. When the aqueous solution is treated with nitric acid and silver nitrate, it yields a white, crystalline precipitate which is not silver chloride; when boiled with alcoholic ammonia and mercuric oxide, the sulphur is not eliminated. The aqueous solution rapidly absorbs bromine, and the sulphur is then oxidised to sulphate. The *sulphate* crystallises in slender needles.

Dithiourimidoacetylacetone, $\text{CH}_2(\text{CMe}\cdot\text{N}\cdot\text{CS}\cdot\text{NH}_2)_2$, was not obtained in the free state. The *hydrochloride* crystallises in yellow scales, melts at 219° , and immediately blackens. The aqueous solution gives a white precipitate with silver nitrate, which dissolves in ammonia with a dark brown coloration. The *sulphate* crystallises in four-sided tablets.

Urimidobenzoylacetone, $\text{COPh}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$, is obtained by adding concentrated hydrochloric acid to an alcoholic solution of benzoylacetone and carbamide. It forms small scales, melts at 191° , and, when treated with hydrochloric acid and then with ammonia, is converted into benzoylacetonecarbamide.

Benzoylacetonecarbamide, $\text{CO}\langle\begin{smallmatrix} \text{N}\cdot\text{CMe} \\ \text{N}\cdot\text{CPh} \end{smallmatrix}\rangle\text{CH}_2$, is obtained either by heating benzoylacetone with carbamide or by treating an alcoholic solution of benzoylacetone and carbamide with hydrochloric acid. The first method does not give good results, and benzoylacetoneamine, biuret, and cyanuric acid are formed. It melts at 228° . The *hydrochloride* sometimes separates out in yellow, rhombic plates. With platinic chloride and hydrochloric acid, it yields the salt



which crystallises in yellow rosettes. When heated with concentrated hydrochloric acid in a sealed tube at 160° , it remains unaltered.

Benzoylacetoneguanidine is obtained by heating a mixture of benzoylacetone and guanidine carbonate. It crystallises in small, sandy aggregates, melts at 173° , and easily yields salts with acids and metallic salts. The *platinochloride* crystallises in small, yellow needles. The solution in hydrochloric acid gives a white precipitate with mercuric chloride, and a soluble precipitate with ferric chloride. The solution in dilute nitric acid gives a crystalline precipitate with silver nitrate. It yields *two sulphates*, crystallising in white nodules and microscopic needles. The hydrochloride and nitrate crystallise in slender needles, the chromate in yellow needles. The *acetyl compound* crystallises in nodules, and melts at 146° . When it is dissolved in acetic acid, treated with nitrous acid, and the mixture poured into water and heated, it yields a brown, crystalline powder which melts at 205° .

The author was unable to obtain a condensation product from phenacetylacetone and carbamide or thiocarbamide.

Phenacetylacetoneguanidine, $\text{NH}\cdot\text{C}\langle\begin{smallmatrix} \text{N}\cdot\text{C}(\text{CH}_2\text{Ph}) \\ \text{N}=\text{CMe} \end{smallmatrix}\rangle\text{CH}_2 + \frac{1}{2}\text{H}_2\text{O}$, is

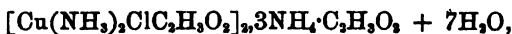
obtained by heating phenacetylacetone with guanidine at 115–120°. It crystallises in needles, and melts at 108°. With platinic chloride and hydrochloric acid, it gives a yellow, crystalline precipitate.

E. C. R.

Cuprammonium Double Salts. By T. W. RICHARDS and H. G. SHAW (*Amer. Chem. J.*, 15, 642–653; compare Abstr., 1892, 953).—*Cuprammonium acetobromide*, $\text{Cu}(\text{NH}_3)_2\text{Br}\cdot\text{C}_2\text{H}_3\text{O}_2$, is formed by treating cupric bromide with alcoholic ammonia, and dissolving the cuprammonium bromide thus formed in alcoholic acetic acid. It forms fairly permanent, deep blue, apparently monoclinic crystals, and has the sp. gr. 2.134.

Ammoniocuprammonium acetochloride, $\text{Cu}(\text{NH}_3)_2\text{Cl}\cdot\text{C}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}$, is prepared by mixing concentrated solutions of copper chloride, acetic acid, and ammonia with alcohol. It forms brilliant, blue crystals of a pearly lustre, and loses ammonia and water slowly on exposure to the air.

Complex cuprammonium acetochloride,



is formed when cupric chloride is treated with a large excess of concentrated ammonia, the excess cautiously neutralised with glacial acetic acid, and the whole treated with alcohol and allowed to evaporate. It forms brilliant, blue crystals of a violet tinge, and although soluble in a small quantity of water, it is decomposed by larger quantities. It decomposes when exposed to the air, losing water and ammonium acetate.

Cuprammonium formobromide, $\text{Cu}(\text{NH}_3)_2\text{Br}\cdot\text{CHO}$, is prepared similarly to the acetic compound.

Cupric ammonic acetochloride, $\text{CuCl}_2\cdot 2\text{NH}_4\cdot\text{C}_2\text{H}_3\text{O}_2$, occurs as a by-product from some of the above preparations. It forms bright green, almost cubical crystals.

Tetrammoniotricuprammonium bromide, $3\text{Cu}(\text{NH}_3)_2\text{Br}\cdot 4\text{NH}_3$, is formed when strong hydrochloric acid is cautiously added to a solution of cupric bromide in the minimum quantity of alcoholic ammonia. It forms deep indigo crystals, and loses ammonia when moist, but is more stable when dry. It is converted by heat (160°) into an olive-green substance, $\text{Cu}(\text{NH}_3)_2\text{Br}$ (Abstr., 1891, 399), which still retains the original crystalline form. Rammelsberg's green, crystalline substance, $\text{CuBr}_2\cdot 5\text{NH}_3$, may have consisted of superficially decomposed crystals of the blue substance.

JN. W.

Syntheses by means of Zinc Chloride. By I. KONDAKOFF (*J. pr. Chem.*, [2], 48, 467–486; compare Abstr., 1893, i, 382).—The compounds of zinc chloride with olefine hydrocarbons have been dealt with (*loc. cit.*). The tertiary alkyl salts may be synthesised from olefines and organic acids in the presence of zinc chloride by keeping the three substances together at 20°; the ethereal salt is subsequently separated by decomposing the zinc chloride compound with water.

In this way tertiary amylic acetate has been prepared; also *tertiary amylic formate*, a colourless liquid which boils at 112–113° (759 mm.), and has a sp. gr. of 0.9086 at 0°, and an odour of amylic

acetate; *tertiary amyllic propionate*, which boils at $142-143.5^{\circ}$ (757.3 mm.), and has a sp. gr. of 0.8769 at 0° ; *tertiary amyllic butyrate*, which boils at 164° (757.3 mm.), and has a sp. gr. of 0.8766 at 0° ; *tertiary amyllic isobutyrate*, which boils at $153-155^{\circ}$ (762 mm.), and has a sp. gr. of 0.8706 at 0° ; *tertiary amyllic isovalerate*, which boils at $173-174^{\circ}$ (762.3 mm.), and has a sp. gr. of 0.8729 at 0° ; *tertiary butylic acetate* (b. p. 51°); and *tertiary hexylic acetate* (b. p. 143° at 757 mm.).

A. G. B.

Action of Ethylic Bromopropionate on Sodium Nitrite.

By G. LEPERCQ (*Bull. Soc. Chim.*, [3], 9, 630—632).—When a mixture of ethylic bromopropionate, absolute alcohol, and sodium nitrite is heated gently on the water bath, it disengages carbonic anhydride, nitrogen, nitric oxide, and ethylic nitrite, and from the solution, a substance, $C_6H_5NO_3$, can be obtained in light, colourless needles of satiny lustre. It is identified with Meyer and Züblin's ethylic nitroso-propionate by the properties of its easily-formed silver salt; its boiling point (213°), however, differs from that (233°) given for the nitrosopropionate. It yields a granular solid nitrosopropionic acid. It is readily oxidised by potassium permanganate, but without the production of ethylnitrolic acid, although a nitrolic acid is obtained with nitrous acid in the ordinary way.

W. T.

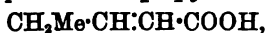
Transformation Products of Normal α -Amidovaleric acid.

By A. MENOZZI and A. PANTOLI (*Gazzetta*, 23, ii, 209—214).—The iodide of potassium α -trimethylamidovalerate, $COOK \cdot C_4H_9 \cdot NMe_3I$, is obtained by heating normal α -amidovaleric acid with methylic iodide in presence of potash. It is very hygroscopic, is soluble in water or alcohol, and crystallises in long, white needles. On adding a solution of iodine in hydriodic acid to its aqueous solution, a *periodide* of the base separates; this is ultimately obtained in well-developed crystals, having a metallic green lustre. When the periodide is suspended in water, and treated with hydrogen sulphide, α -trimethylamidovaleric acid iodide is obtained; this separates from dilute hydriodic acid in monosymmetric crystals containing $2H_2O$, $a : b : c = 1.4852 : 1 : 1.2459$; $\beta = 80^{\circ} 33'$. It melts at $181-182^{\circ}$, is stable in the air, and soluble in water or alcohol. On crystallising it from alcohol, an iodide of the composition $(COOH \cdot C_4H_9 \cdot NMe_3)_2I$ is obtained, crystallising in cubes.

On treating the iodide melting at $181-182^{\circ}$ with silver chloride, α -trimethylamidovaleric acid chloride, $COOH \cdot C_4H_9 \cdot NMe_3Cl$, is obtained; it forms small, transparent prisms, and is soluble in water or alcohol. With platinic chloride, it yields a *methylic platinumchloride* of the composition $(COOH \cdot C_4H_9 \cdot NMe_3)_2 \cdot Me_3PtCl_5 \cdot 2H_2O$; this forms yellow prisms which lose water at 100° and melt at 219° . The *methylic aurochloride*, $COOH \cdot C_4H_9 \cdot NMe_3 \cdot MeAuCl_4$, is obtained in anhydrous, yellow laminæ which melt at 160° .

On treating the iodide of the potassium salt described above with moist silver oxide in aqueous solution, silver iodide is deposited: this is filtered off, the alkaline solution concentrated, and the residue

heated at 120°. Trimethylamine is evolved, and, on treating the product with dilute sulphuric acid, *propylideneacetic acid*,



is liberated; this is a colourless oil which boils at 194—195°, and remains liquid at -16°; it has an odour resembling that of α -crotonic acid. It is heavier than water at 0°, but lighter at 15°. The propylideneacetic acid prepared by Ott (Abstr., 1891, 1453) and others does not coincide in properties with the authors' product; several of the salts of the acid are described. During the preparation of this acid, a small quantity of normal α -hydroxyvaleric acid is obtained.

W. J. P.

Composition of Rape Oil. By G. PONZIO (*J. pr. Chem.*, [2], 48, 487—488).—Reimer and Will (Abstr., 1887, 1030) state that rape oil contains the glycerides of erucic and rapic acids, in about equal proportions, and a little behenic acid. The author shows that their behenic acid is arachidic acid, which the oil contains to the extent of about 4 per cent. Arachidamide melts at 108° (compare Schweizer, Abstr., 1885, 508).

A. G. B.

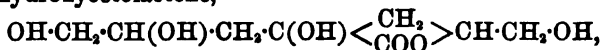
A Nitrogenous Acid in Beet Juice. By E. O. v. LIPPMANN (*Ber.*, 26, 3061—3063).—A yellow, crystalline deposit was obtained while working up the juice of beets which had been frozen and thawed. The author has isolated from this deposit an acid which he believes to be citrazinic acid, $\text{C}_6\text{H}_2\text{NO}_4$. It is a yellow, crystalline powder, scarcely soluble in boiling water, decomposes at 300° with an odour resembling that of burning hair, and is soluble in alkalis and alkali carbonates.

E. C. R.

Oxidation of Diallyloxalic acid with Potassium Permanganate. By S. FOKYN (*J. pr. Chem.*, 48, 522—533).—Bulitsch has shown that a tetrahydroxyoctolactone is obtained by oxidising diallyloxalic acid with nitric acid. On the other hand, Schutzky could not obtain this lactone by oxidising with permanganate; the author, however, finds that by careful oxidation with this agent, under conditions detailed in the original paper, the lactone is obtained together with a lactonic acid.

The *lactonic acid*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\langle\text{CH}_2\rangle_{\text{O}\cdot\text{CO}}\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{COOH}$, is a yellowish syrup, and has a sour taste. The *calcium salt*, $\text{C}_7\text{H}_{10}\text{O}_7\text{Ca}$, and the *barium salts*, $\text{C}_7\text{H}_{10}\text{O}_7\text{Ba}$ and $(\text{C}_7\text{H}_9\text{O}_6)_2\text{Ba}$, are described.

Tetrahydroxyoctolactone,



is a syrup and has a sweet taste. The *calcium salt*, $(\text{C}_8\text{H}_{16}\text{O}_7)_2\text{Ca} + 2\text{H}_2\text{O}$, and *barium salt*, $(\text{C}_8\text{H}_{16}\text{O}_7)_2\text{Ba}$, a yellowish, glassy, hygroscopic mass, melting at 84°, were obtained. This lactone differs from the compound obtained by the oxidation of diallyloxalic acid with nitric acid as shown by a comparison of the salts. The calcium and barium

salts, $(C_8H_{13}O_7)Me''$, obtained by Bulitsch are glassy, whereas the calcium salt obtained by the author is crystalline. These two salts, moreover, cannot be converted into salts of the composition $(C_8H_{13}O_6)_2Me''$; the author's lactone does not yield basic salts $C_8H_{13}O_6Me''$ and $(C_8H_{13}O_7)_2Me''$, even when boiled with the alkaline earths. Finally, Bulitsch's lactone yields an insoluble lead salt, whereas the lead salt of the above lactone is soluble. E. C. R.

Ethereal Salts of Oxalacetic acid. By W. WISLICENUS and A. GROSSMANN (*Annalen*, 277, 375—383).—*Methylic oxalacetate*, $COOMe \cdot CO \cdot CH_2 \cdot COOMe$, is prepared by adding methylic oxalate together with ether to solid sodium methoxide, and subsequently heating the mixture with methylic acetate on the water bath; the sodium derivative thus obtained is decomposed by dilute sulphuric acid. The methylic salt crystallises in colourless, lustrous needles, melts at $74-76^\circ$, and boils at 137° under 39 mm. pressure; the alcoholic solution gives a red colour with ferric chloride. The copper derivative, $(C_8H_7O_5)_2Cu$, forms small, green needles, and melts at $214-215^\circ$ with decomposition. The phenylhydrazone, already described by Buchner (*Abstr.*, 1890, 156), yields *methylic phenylpyrazolonecarboxylate*, $COOMe \cdot C \begin{smallmatrix} N-NPh \\ \diagup \quad \diagdown \\ CH_2 \quad CO \end{smallmatrix}$, when heated above its melting point; this forms white crystals, and melts at 197° .

Amylic oxalacetate, $COO(C_8H_{11}) \cdot CO \cdot CH_2 \cdot COO \cdot C_8H_{11}$, is obtained by adding amylic oxalate and ether to solid sodium ethoxide, and subsequently amylic acetate, and decomposing the sodium compound with dilute acid. It is an oil having an unpleasant odour, boils at 167° under a pressure of 23 mm., and the alcoholic solution gives a deep red coloration with ferric chloride; it yields an oily *phenylhydrazone*, which condenses to *amylic phenylpyrazolonecarboxylate* when heated at 190° . The copper derivative melts at $83-85^\circ$.

Methylic ethylic oxalacetate, $COOMe \cdot CH_2 \cdot CO \cdot COOEt$, prepared from ethylic oxalate and methylic acetate as in the above cases, is a colourless oil boiling at 130° (22 mm.), and at 124° (16 mm.); the copper derivative melts at $134-135^\circ$. When the *phenylhydrazone* is heated, it is converted into *ethylic phenylpyrazolonecarboxylate*, $COOEt \cdot C \begin{smallmatrix} N-NPh \\ \diagup \quad \diagdown \\ CH_2 \quad CO \end{smallmatrix}$, melting at $180-182^\circ$. A. R. L.

Preparation of Amides. By A. VERLEY (*Bull. Soc. Chim.*, [3], 9, 690—692).—Distillation of dry potassium or sodium salts of the organic acids with ammonium (or a replaced ammonium) chloride gives a better yield of the corresponding amides than distillation of the ammonium salts directly, and the product is readily purified. In this way 80 per cent. of the theoretical yield of acetamide has been obtained.

Methylamine hydrochloride distilled with potassium acetate and a little acetic acid gives 88 per cent. of the theoretical yield of methylacetamide. Similarly, a yield of 91 per cent. of dimethylacetamide is obtained. With formamide, the yield is 78 per cent. Succinimide

requires the ammonium chloride and potassium succinate to be intimately mixed. The yield of product, purified by recrystallisation after treatment with animal black, is 87 per cent. of the theoretical.

Dimethylformamide.—This substance is prepared exactly like dimethylacetamide. It is a liquid of a feeble but not disagreeable odour, boiling without decomposition at 155° ; sp. gr. 0.968 at 20° .

W. T.

Formation of Dithienyl Derivatives from Thiophen. By A. TÖHL and O. EBERHARD (*Ber.*, 26, 2945—2947).—When sulphuryl chloride is mixed with thiophen and a small quantity of aluminium chloride added, a violent action takes place, sulphurous anhydride and hydrogen chloride being evolved. The residue contains small quantities of chlorothiophen, but consists chiefly of a mixture of trichlorodithienyl and dichlorodithienyl. *Trichlorodithienyl*, $C_8S_2H_2Cl_3$, forms short needles, and melts at 103° ; it is converted by the action of bromine into *trichlorotribromodithienyl*, $C_8S_2Cl_3Br_3$, which crystallises in long, pale yellowish needles, and melts at 214 — 215° . *Dichlorodithienyl*, $C_8S_2H_2Cl_2$, forms thin, yellowish plates, melts at 109 — 110° , and, on treatment with bromine, yields *dichlorotetrabromodithienyl*, $C_8S_2Cl_2Br_4$, which crystallises in reddish needles, and melts at 221 — 222° .

H. G. C.

Action of Sulphuric acid on Chlorothiophen. By A. TÖHL and O. EBERHARD (*Ber.*, 26, 2947—2949).—The presence of small quantities of chlorothiophen in the product of the action of sulphuryl chloride on thiophen in presence of aluminium chloride (see preceding abstract) leads to the supposition that this is the first product of the action, and that it undergoes condensation to dithienyl derivatives in presence of sulphuryl chloride. The authors have therefore endeavoured to bring about the same condensation by treating chlorothiophen with concentrated sulphuric acid. The α -chlorothiophen is obtained in much larger quantity from sulphuryl chloride and thiophen if the mixture is diluted with ether, and may be readily prepared in this manner. When treated with sulphuric acid, it is converted chiefly into *chlorothiophensulphonic acid* and *chlorodithienyl*, $C_8S_2H_2Cl$, but the latter could not be obtained quite pure; with bromine this yields *chloropentabromodithienyl*, $C_8S_2ClBr_5$, which crystallises in long, white needles, and melts at 238 — 240° . The barium salt of chlorothiophensulphonic acid, $(C_8SH_2ClSO_3)_2Ba + 2H_2O$, crystallises from alcohol in small druses of white needles.

H. G. C.

New Method of preparing Iodochlorides. By A. TÖHL (*Ber.*, 26, 2949—2950).—A very good yield of the iodochlorides may be obtained by treating the iodo-derivative with sulphuryl chloride in ethereal solution, the presence of a little water being necessary to start the reaction. Satisfactory results have been obtained by this method with iodobenzene, piodotoluene, 1:3:4-iodometaxylene, and iodomesitylene.

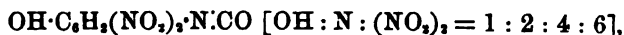
H. G. C.

Electrolytic Reduction of Nitrobenzene. By C. HAEUSSERMANN (*Chem. Zeit.*, 17, 129 and 209).—This paper was published prior to those of Gattermann and Koppert (*Abstr.*, 1893, i, 567; this vol., i, 72). The reduction of nitrobenzene in alkaline solution is carried out as follows:—Nitrobenzene (25 grams) dissolved in alcohol (350 c.c.) and mixed with a solution of sodium hydroxide (40 grams) in water (50 c.c.) is introduced into a porous cell which contains the cathode (iron or platinum, according to the nature of the solution); the porous cell stands in an outer vessel containing a platinum or carbon anode and filled with dilute sodium hydroxide. A current of 6–8 ampères at a potential of 6 volts is used. The precipitation of hydrazobenzene at the cathode soon commences, and at the end of 10 hours benzidine is obtained. Orthonitrotoluene yields the corresponding compounds, but in smaller quantity than nitrobenzene. If the reduction is conducted in acid solution, the porous cell is charged with nitrobenzene (25 grams), sulphuric acid (30 grams), water (100 c.c.), and alcohol (350 c.c.). The current used is 5 ampères at a potential of 4.5 volts. Benzidine sulphate soon commences to separate at the cathode, and on adding water to the filtrate azoxybenzene is precipitated. When the solutions are previously heated to 60°, traces of aniline are also formed, whereas the greater portion of the nitrobenzene remains unaltered, so that the electrolytic production of aniline seems impracticable; the same may be said of that of ortho- and para-toluidine. When, however, a solution of metanitrobenzenesulphonic acid in dilute sulphuric acid is submitted to a current of 3 ampères at a potential of 4 volts, metanilinesulphonic acid is obtained.

A. R. L.

Action of Carbonyl Chloride on Picramic acid. By F. RUDOLF (*J. pr. Chem.*, [2], 48, 425–446).—Finely powdered picramic acid, m. p. 168–169° (uncorr.), was heated at 130–140° for 4–5 hours with a 15 per cent. solution of carbonyl chloride in chloroform, in a sealed tube. The solid product of the reaction was washed with chloroform and crystallised from water.

The *hydroxydinitrophenyl isocyanate*,



thus obtained, crystallises in small, nearly white, obliquely truncated prisms, and in long needles. It melts at 222–223° (uncorr.), and dissolves very sparingly in cold water, more freely in hot water, ether, acetone, concentrated sulphuric acid, and glacial acetic acid, sparingly in benzene, and not at all in chloroform. Its solutions are acid; when heated with water for some hours, it is hydrolysed into picramic acid and carbonic anhydride. The *sodium*, *potassium*, and *silver* derivatives, corresponding with the formula



were prepared.

When the isocyanate is heated with ammonia in aqueous or alcoholic solution, the *ammonium* derivative of *carbamidodinitrophenol*, $\text{NH}_4\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is obtained in the form of small, thick,

red prisms. The carbamidodinitrophenol, liberated by acidifying the ammonium salt, is identical with Griess' uramidodinitrophenylic acid (*J. pr. Chem.*, [2], 5, 1); by hydrolysis, it is converted into the original isocyanate and ammonia.

With aniline, the isocyanate forms *phenylcarbamidodinitrophenol*, $\text{OH}\cdot\text{C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, which crystallises in microscopic, red prisms, and decomposes at 200° . With phenylhydrazine, *phenylhydrazine carbamidodinitrophenol phenylhydrazide*,



is produced; it crystallises in orange needles, and decomposes at 130° ; when heated with solvents, it loses phenylhydrazine, becoming *phenylhydrazinecarbamidodinitrophenol*, $\text{OH}\cdot\text{C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{NH}\cdot\text{CO}\cdot\text{N}_2\text{H}_5\text{Ph}$, which crystallises in microscopic needles, and melts with decomposition at $202\text{--}203^\circ$.

By heating the isocyanate with alcohol, *ethylic hydroxydinitrophenylcarbamate* is obtained; this crystallises in yellow needles, melts at 153° , and dissolves in the usual organic solvents except light petroleum. When heated with hydrochloric acid, it yields ethylic chloride, carbonic anhydride, and picramic acid hydrochloride. The *ammonium*, *potassium*, and *silver* derivatives are described. The corresponding *methylic salt*, analogously prepared, crystallises in yellow needles, and melts at 179° (uncorr.). A. G. B.

Action of Sodium on γ -Bromopropylphenyl Ether. By W. SALONINA (*Ber.*, 26, 2987—2988).—The author describes the preparation of hexamethylene derivatives from γ -bromopropylphenyl ether. The latter substance, when heated with sodium, yields, in addition to sodium phenoxide, a small amount of hexamethyleueglycoldiphenyl ether, $\text{OPh}\cdot\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{CH}_2\cdot\text{OPh}$, which crystallises from alcohol in long needles, melts at 83° , and is only slightly soluble in cold alcohol. When this ether is heated with concentrated hydrobromic acid at 150° , it is converted into hexamethylene dibromide, $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_4\cdot\text{CH}_2\text{Br}$, which boils at $240\text{--}247^\circ$ without decomposition. Hydriodic acid at 110° converts the diphenyl ether into the corresponding diiodide, $\text{CH}_2\text{I}\cdot[\text{CH}_2]_4\cdot\text{CH}_2\text{I}$, which is an almost colourless liquid, decomposes on distillation, and solidifies, on cooling, to a mass which melts at -7° . The author is continuing his investigations. A. H.

Compounds of Picric acid with Phenols and Ketones. By R. v. GORDIKE (*Ber.*, 26, 3042—3046).—The compounds are obtained by adding a hot saturated solution of picric acid in 50 per cent. alcohol to a similar solution of the phenol. A small excess of phenol is used, to prevent the compound being contaminated with picric acid. The picrates are somewhat stable, but decompose when heated at 100° or in a desiccator over sulphuric acid. They are also decomposed by boiling with ammonia or soda.

Phenol picrate, $\text{C}_6\text{H}_5\cdot\text{OH}\cdot 2\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, crystallises in bright yellow needles, and melts at 53° .

Orthocresol picrate, $2\text{C}_6\text{H}_4\cdot\text{OH}\cdot 3\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, crystallises in orange

needles, and melts at 88°. Neither metacresol nor paracresol combines with picric acid.

Ortho-xylenol picrate, $5C_6H_5 \cdot OH, 4C_6H_5N_3O_7$, forms orange crystals, and melts at 82°. Paraxylenol also yields a picrate; metaxylenol does not.

Of the dihydroxybenzenes, only pyrocatechol combines with picric acid. The *picrate*, $C_6H_4(OH)_2, C_6H_5N_3O_7$, crystallises in orange needles, and melts at 122°.

Guaiacol picrate crystallises in beautiful, orange needles, and melts at 86°. *Creosol picrate* crystallises in yellow needles, and melts at 96°. *Ethylguaiacol picrate* crystallises in orange needles, and melts at 90°. *Propylguaiacol picrate* crystallises in red needles, and melts at 59°.

Pyrogallol and phloroglucinol do not yield picrates. *Dimethylpyrogallol picrate* crystallises in yellow needles, and melts at 53°.

Orthochlorophenol picrate, $C_6H_4Cl \cdot OH, C_6H_5N_3O_7$, crystallises in bright yellow needles, and melts at 81–82°.

Acetophenone picrate, $COMePh, C_6H_5N_3O_7$, forms greenish yellow, quadratic crystals, and melts at 53°.

Gallacetophenone picrate crystallises in orange needles, and melts at 133°.

The author draws attention to the fact that, as a rule, it is only the ortho-compounds which are able to form picrates. E. C. R.

Essence of Tarragon and its Conversion into Anethoil. By E. GRIMAUD (*Compt. rend.*, 117, 1089–1092).—When essence of tarragon is subjected to fractional distillation, about 60 per cent. boils between 210° and 215°, and after four distillations this product boils between 210.5° and 212° under a pressure of 747.4 mm. Neither the crude essence nor the purified product contains any anethoil.

Estragoil $C_{10}H_{12}O_2$, the chief constituent of essence of tarragon, boils at 215–216° (corr.); sp. gr. at 15° = 0.9325; index of refraction for D = 1.523. Its boiling point is 16–17° below that of anethoil.

Estragoil is easily converted into anethoil by heating it on a water bath for about 24 hours with three or four times its weight of concentrated alcoholic potash, and the product is identical with the anethoil obtained from the oil of aniseed.

It would seem that estragoil and anethoil differ in the isomerism of the group C_3H_5 , the constitution of the former being



and of the latter $OMe \cdot C_3H_4 \cdot CH \cdot CHMe$, the difference being the same as that which exists between eugenol and isoegenol, safrole and isosafrole. The difference between the boiling points of the two isomerides is practically the same in all three cases.

The methyl derivative of the chavicol obtained by Eykmann from the oil of the betel nut boils at 226°, and is probably a stereoisomeride of anethoil, and not a propenylic derivative like estragoil.

C. H. B.

Condensation Products of Monobasic acids with Resorcinol. By G. COHN (*J. pr. Chem.*, [2], 48, 384–410; compare *Abstr.*, 1893, i, 719).—The following conclusions are drawn:—(1) Monobasic

acids condense with resorcinol, under certain conditions, to form fluoresceins. (2) The character of these colouring matters is independent of the nature of the acid, for they are all similar in colour, fluorescence, spectrum, solubility, and in the nature of their derivatives. (3) All give similar tetrabromo-substitution products, eosins containing the bromine in the resorcinol nucleus. (4) The influence of the acid is exhibited in the facts that (a) aliphatic fluoresceins show a smaller affinity for animal fibres than do aromatic fluoresceins; and (b) the more complex acids yield more highly halogenised, redder derivatives. (5) Benzoic acid and benzotrichloride, with resorcinol and zinc chloride, yield the same colouring matter, whilst benzaldehyde gives a product which differs from the benzeins.

A. G. B.

Reaction of Sodium Alkyl oxides with Tribromotrinitrobenzene. By C. L. JACKSON and W. H. WARREN (*Amer. Chem. J.*, 15, 607—642; compare Abstr., 1891, 1024).—With sodium ethoxide, tribromotrinitrobenzene yields diethyltribromonitroresorcinol, triethyltrinitrophloroglucinol, and the products of hydrolysis of the latter.

Diethyltribromonitroresorcinol is converted by boiling alcoholic sodium hydroxide, with elimination of bromine, into *diethylbromonitroresorcinol* $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{Br}(\text{OEt})_2$, a substance crystallising in long, silky, white needles, and melting at 115° .

Triethyltrinitrophloroglucinol, $\text{C}_6(\text{NO}_2)_3(\text{OEt})_3$, crystallises in long, slender plates, turns brown on exposure to the air, and melts at $119\text{--}120^\circ$. It is hydrolysed by alcoholic sodium hydroxide into *diethyltrinitrophloroglucinol*, $\text{OH}\cdot\text{C}_6(\text{NO}_2)_3(\text{OEt})_2$, and *trinitrophloroglucinol* with H_2O . The former crystallises in straw-coloured needles or prisms, and melts at 89° . It decomposes alkaline carbonates; the sodium salt crystallises in fine, orange-red needles. The latter crystallises in yellow, hexagonal prisms, and, when free from water, melts at 167° . The low melting point (158°) found by Benedikt (*Ber.*, 11, 1376) was probably due to imperfect dehydration. The two substances are formed in the preparation of the triethyl compound if moisture is not excluded, the hydrolysis being effected by sodium hydroxide formed by the action of moisture on the sodium ethoxide. The influence of benzene on the relative proportion of the phloroglucinol and resorcinol compounds was investigated, and it was found that less nitrous acid (33.5 per cent. of the theoretical) was evolved, and therefore less resorcinol compound formed, when benzene was present than when alcohol alone was used (45.9 per cent.). In the presence of ethylic acetate, the principal product was dinitrophenetol, m. p. 147° , the formation of which was probably due to the hydrolysis of the resorcinol compounds, since when the solvents were previously dried the yield was much less.

By the action of a solution of sodium methoxide in methylic alcohol on tribromotrinitrobenzene, dimethyltribromonitroresorcinol (*loc. cit.*) is formed together with *dimethyltrinitrophloroglucinol*, crystallising in yellowish needles, and melting at $77\text{--}78^\circ$. The alkali salts are yellow.

Sodium propoxide in the presence of alcohol and benzene yields

tripropyltrinitrophloroglucinol, a substance crystallising in yellow prisms, and melting at 109—110°. The corresponding *isopropyl compound* crystallises in colourless prisms, and becomes orange on exposure to the air; it melts at 130°. Sodium isobutoxide and isoamyloxide also react with tribromotrinitrobenzene, but the products were not examined. Nitrite as well as bromide was formed in all the above cases; the relative amount of nitrite tended to diminish as the molecular weight increased.

Sodium benzyloxide in benzylic alcohol solution (prepared by dissolving sodium in benzylic alcohol) yields, with a benzene solution of tribromotrinitrobenzene, *tribenzyltrinitrophloroglucinol* and trinitrophloroglucinol. The former substance crystallises in white needles and is discoloured by the air; it melts at 171°. A small quantity of benzylic bromide is also formed. Since this substance is without action on the sodium salt of trinitrophloroglucinol, its presence may be due to the direct action of the sodium benzyloxide on the trinitro-tribromobenzene.

Triphenyltrinitrophloroglucinol, $C_6(NO_2)_3(OPh)_3$, is converted by alcoholic sodium ethoxide into the corresponding ethyl compound, with elimination of phenol. JN. W.

Some Peculiar Cases of Isomerism. By R. FABINYI (*Zeit. physikal. Chem.*, 12, 564—582).—When asarone is dissolved in absolute alcohol, and amylic nitrite and then alcoholic hydrogen chloride are added to the cooled solution, green prisms (m. p. 159.4°) of asarylaldoxime hydrochloride are obtained. If, however, the alcoholic hydrogen chloride be added first, and then the amylic nitrite, red prisms are formed which melt at 161.6°. These, on analysis, were found by the author to give numbers also corresponding with asarylaldoxime hydrochloride, and were thus isomeric with the green prisms. The free aldoximes from these salts are both anti-aldoximes; they differ very slightly from each other, and give acetyl compounds which are still more similar, one and the same aldoxime being regenerated from the two acetyl derivatives. The hydrochlorides, on repeated recrystallisation from glacial acetic acid, approximate gradually to each other in colour, melting point, and solubility, the final substance obtained from both being golden yellow, and melting at 155.5°. The hydrochloride of the aldoxime prepared directly from asarylaldehyde crystallises in golden yellow needles which melt at 155.4°.

Several other examples of similar cases of isomerism are alluded to. J. W.

New Formation of Secondary Aromatic Amines. By V. MERZ and S. PASCHKOWEZY (*J. pr. Chem.*, [2], 48, 454—466).—The method consists in heating halogen benzene hydrocarbons with primary amines and a strong inorganic base. In this way, phenylparatolylamine is obtained from bromo-, chloro-, and iodo-benzene respectively, and paratoluidine; also from parabromo- and pariodotoluene respectively, and aniline. Phenylorthotolylamine is obtained from bromobenzene and orthotoluidine; diphenylamine from bromobenzene and excess of aniline; diparatolylamine from parabromo-

toluene and paratoluidine; and aniline from bromobenzene and ammonia. A. G. B.

Isomerism in the Azo-Series. By J. T. HEWITT (*Ber.*, 26, 2975—2978).—*Orthochlorobenzeneazophenol*, $C_6H_4Cl \cdot N=N \cdot C_6H_4 \cdot OH$, prepared by treating a mixture of orthochloraniline nitrate and phenol with potassium nitrite, is precipitated from alcoholic solution by the addition of water in fine, yellow needles melting at 85° . It is very readily soluble in the usual organic solvents, but almost insoluble in water, and is precipitated from its solution in alkalis by carbonic anhydride. When heated for an hour at 80° , it is converted into a light red substance of the same composition, melting at 96° . This modification behaves in the same way towards solvents as the yellow form, but the latter is precipitated by acids from its solutions in alkalis, and by water from alcoholic solution. This behaviour might be accounted for either by tautomerism as expressed in the formulæ $C_6H_4Cl \cdot N=N \cdot C_6H_4 \cdot OH$ and $C_6H_4Cl \cdot NH \cdot N \cdot C_6H_4 \cdot O$, or by geometrical isomerism, $\begin{matrix} C_6H_4Cl \cdot N \\ \parallel \\ OH \cdot C_6H_4 \cdot N \end{matrix}$ and $\begin{matrix} C_6H_4Cl \cdot N \\ \parallel \\ N \cdot C_6H_4 \cdot OH \end{matrix}$. Both the modifications when treated with acetic anhydride yield the same *acetate*, which crystallises in fine yellow needles, and melts at 100° . It is insoluble in water, readily soluble in alcohol, &c. The *benzoate* crystallises from hot alcohol in yellow plates, melting at 131° .

Metachlorobenzeneazophenol crystallises from dilute alcohol in splendid, brownish-violet needles, which, after heating at 80° , become pale yellow, and then melt at 135° . The *acetate* separates from dilute alcohol in yellowish-red plates melting at 92° . The *benzoate* forms yellow scales, and melts at 118° .

Parachlorobenzeneazophenol, which was previously known, does not yield an isomeric form when heated. Its *acetate* crystallises from alcohol in hair-like, yellow needles, and melts at 160° . The *benzoate* forms small, yellowish-red plates melting at 154° . A. H.

Diazosulphides. By P. JACOBSON (*Annalen*, 277, 209—218).—An introductory paper (see following abstracts and p. 137). The orthodiazosulphides, unlike the orthodiazooxides, are colourless compounds resembling in this respect the azimides obtained by the action of nitrous acid on the orthodiamines. They generally crystallise well, have a characteristic, sweetish odour, and are very feebly basic. The first representative of the class, chlorophenylene diazosulphide, was obtained by Beilstein and Karbatow (*Annalen*, 179, 82). Bernthsen (*Abstr.*, 1889, 775) described another member of the group, namely, diazothiodimethylaniline, whilst the simplest members were prepared by the author (*Abstr.*, 1889, 135 and 772).

A. R. L.

Phenylene Diazosulphide and its Derivatives. By P. JACOBSON and H. JANSSEN (*Annalen*, 177, 218—231).—Phenylene diazosulphide, $C_6H_4 \cdot \begin{matrix} N \\ \parallel \\ S \end{matrix} \cdot N$ (*Abstr.*, 1889, 135), is prepared by the action of nitrous acid on amidophenyl mercaptan. The compound melts at $35.5\text{--}36^\circ$,

when heated in a capillary tube, whilst by introducing a thermometer into a quantity of the fused substance the solidifying point (?) was found to be 34.95° ; it boils at 129° (corr.) under a pressure of 10 mm., and at 188° (corr.) under a pressure of 150 mm. It is insoluble in dilute acids, but dissolves in concentrated hydrochloric acid, being reprecipitated on dilution with water; a molecular weight determination by the cryoscopic method established the above formula. A quantity of the compound (0.3–0.5 gram) dissolved in 5 per cent. alcohol and injected subcutaneously into a rabbit causes death in 48 hours; the toxic phenomena consist in the gradual paralysis of the central nervous system accompanied by a continuous lowering of the temperature. The *platinochloride*, $(C_6H_4N_2S)_2H_2PtCl_4$, forms small, six-sided tablets; a crystalline additive compound, $C_6H_4N_2S.HgCl_2$, was also obtained. Phenylene diazosulphide remains unaltered when heated in sealed tubes with alcohol at 150 – 160° , with 20 per cent. potash at 150° , and with 27 per cent. sulphuric acid at 200° , or when boiled with alcoholic ammoniacal silver solution. When boiled with tin and hydrochloric acid, orthoamidophenyl mercaptan is formed, whilst, if treated with oxidising agents, the greater portion remains unaltered, and the remainder appears to undergo complete combustion. When heated at 200 – 250° until gas ceases to be evolved, the residue consists of diphenylene bisulphide, $C_6H_5<\underset{S}{\overset{S}{>}}C_6H_5$.

Methylphenylenediazosulphine iodide, $\begin{matrix} C_6H_5 \cdot N \\ SMeI \end{matrix} > N$, is prepared by heating phenylene diazosulphide with an excess of methylic iodide in a sealed tube at 100° ; it crystallises from water in red needles. The compound $\begin{matrix} C_6H_5 \cdot N \\ SEtI \end{matrix} > N$ forms stout, red prisms.

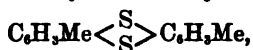
Methylphenylenediazosulphine chloride, $\begin{matrix} C_6H_5 \cdot N \\ SMeCl \end{matrix} > N$, is obtained by digesting a solution of the iodide with silver chloride; it crystallises in colourless, hydrated prisms. When concentrated solutions of ammonium picrate are added to those of the iodide, double decomposition ensues, and crystalline picrates are precipitated.

A. R. L.

Homologues of Phenylene Diazosulphide. By P. JACOBSON and E. NEY (*Annalen*, **277**, 232–236).—The homologues of phenylene diazosulphide are prepared from the ethenyl compounds of the corresponding amidomercaptans (compare Abstr., 1889, 772); the latter being heated with alcoholic potash in sealed tubes at 180 – 190° , and the resulting amidomercaptans treated with nitrous acid.

Tolylene diazosulphide, $C_6H_4Me<\underset{S}{\overset{N}{>}}N$ [$Me : S : N = 1 : 3 : 4$], crystallises in colourless tables, melts in a capillary tube at 42 – 43° , and distils without decomposition under diminished pressure; the solidifying point (?) determined with a large quantity of the fused substance is 40.9° . On reduction with tin and hydrochloric acid,

it behaves in an analogous manner to phenylene diazosulphide, and, when heated at 200—220°, it yields *ditoluylene bisulphide*,



which crystallises in faintly yellowish needles, and melts at 116°; *methyltoluylene-sulphine iodide* forms beautiful golden-yellow prisms.

Xylylene diazosulphide, $\text{C}_6\text{H}_4\text{Me}_2 \langle \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \rangle \text{N}$ [$\text{Me}_2 : \text{N} : \text{S} = 1 : 3 : 4 : 5$], crystallises in lustrous needles, and melts at 37°; *di-xylylene bisulphide*, $\text{C}_6\text{H}_4\text{Me}_2 \langle \begin{smallmatrix} \text{S} \\ \text{S} \end{smallmatrix} \rangle \text{C}_6\text{H}_4\text{Me}_2$, prepared by heating it at 250°, melts at 118°. Xylylene diazosulphide shows little tendency to combine with methylic iodide, and, when heated in a sealed tube at 100° with it, only a very small quantity of a compound soluble in water is obtained.

Cumylene diazosulphide, $\text{C}_6\text{HMe}_3 \langle \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \rangle \text{N}$, crystallises in prisms, and melts at 85°; its odour is faint and not characteristic, and it loses its nitrogen at a higher temperature (270°) than the lower homologues, but a homogeneous substance could not be isolated from the residue.

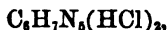
A. R. L.

Substitution Derivatives of Phenylene Diazosulphide. By P. JACOBSON and A. KWATSSER (*Annalen*, 277, 237—256).—*Nitro-carbimidothiophenol*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \langle \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \rangle \text{C} \cdot \text{OH}$, is thus prepared. Phenylthiocarbimide is boiled for 18 hours with absolute alcohol, and the phenylthiourethane thus formed is oxidised with alkaline potassium ferricyanide (see *Abstr.*, 1886, 876). The product, ethoxyphenylthiocarbimide, is then hydrolysed with hydrochloric acid, whereby carbimidothiophenol is obtained, which is dissolved in glacial acetic acid, and treated in the cold with nitric acid of sp. gr. 1.52. The nitro-derivative crystallises in stellate aggregates of light yellow needles, and melts at 252°. When an excess of soda is added to its solution in dilute soda, the *sodium* salt separates as a yellow, crystalline precipitate. The *ethylic* salt forms faintly yellow, silky needles, and melts at 205°.

Nitramidophenyl mercaptan, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{SH}$ [$\text{NO}_2 : \text{NH}_2 : \text{SH} = 5 : 2 : 3$] (Mylius, *Inaug. Diss.*, 1883), is obtained by heating nitro-carbimidothiophenol with aqueous ammonia of sp. gr. 0.95 in a sealed tube at 160—170°; it forms microscopic, pale yellow needles, melts at 83—84°, and is oxidised when exposed in the moist condition to the air, forming the bisulphide, $\text{S}_2[\text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{NO}_2]_2$; this compound is, however, best prepared by oxidising the mercaptan with ferric chloride; it crystallises in lemon-yellow needles, and melts at 236—237°. When the mercaptan is digested with concentrated formic acid, the methenyl derivative, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \langle \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \rangle \text{CH}$ (Mylius, *loc. cit.*), melting at 176—177°, is produced.

Nitrophenylene diazosulphide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \langle \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \rangle \text{N}$, is obtained by the

its composition and mode of formation, must be *diamidoazimidobenzene*. It has only been obtained in the form of the *dihydrochloride*,



as the free base rapidly oxidises in the air; the solution of the salt, when treated with an orthodiketone such as croconic acid or glyoxal, yields azines, proving that the two amido-groups are combined with adjacent carbon atoms, the diamidoazimidobenzene having therefore the constitution $\text{H}_2\text{N} > \text{C}_6\text{H}_4 < \text{N} \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} > \text{N}$. Whether the amido-groups occupy the 1 : 2- or 2 : 3-position is uncertain, but the authors regard the latter as the more probable.

By the action of nitrous acid on the diamido-compound, the two amido-groups are converted in the usual manner into an azimido-group, *diasimidobenzene*, $\text{N} < \text{N} \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} > \text{C}_6\text{H}_4 < \text{N} \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} > \text{N}$, being formed.

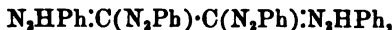
After purification, this forms colourless needles melting above 300° ; it is an extremely stable substance, and may be dissolved in concentrated nitric acid, and reprecipitated unaltered by the addition of water.

H. G. C.

Constitution of the Amido-derivatives of Hydroxylamine. By G. MINUNNI and G. ORTOLEVA (*Gazzetta*, 23, ii, 237—244; compare Minunni, Abstr., 1891, 697).—On heating dibenzhydroxamic acid with phenylhydrazine on the water bath, benzoylphenylhydrazine and a little benzoic acid are obtained. The reaction probably proceeds in two stages, in the first of which benzoylphenylhydrazine and benzhydroxamic acid are formed, whilst in the second stage the latter reacts with more phenylhydrazine, giving the benzoyl derivative and hydroxylamine. On gently heating dibenzhydroxamic acid with aniline, benzanilide is obtained, whilst with paratoluidine the oxamic acid yields benzoylparatoluidide; in these cases also, the action would seem to proceed in two stages. These results can only be explained by assigning the constitution $\text{NHBz} \cdot \text{OBz}$ to dibenzhydroxamic acid; the formula proposed by Lossen would indicate a very different behaviour under such treatment.

W. J. P.

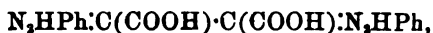
* **Diformazyl and its Relations to Diamidrazone.** By E. BAMBERGER and F. KUHLEMANN (*Ber.*, 26, 2978—2982; compare Abstr., 1893, i, 84).—When acids containing the group $-\text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}-$ are treated with an excess of alkaline diazobenzene, they are decomposed, with formation of *diformazyl*,



along with other products. Thus levulinic acid,



yields acetic acid, carbonic anhydride, and diformazyl; acetonediacetic acid (hydrochelidonic acid), $\text{CO}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH})_2$, yields the same substance along with carbonic anhydride and succinic acid, whilst the osazone of dihydroxytartaric acid (tartrazin),



gives this same compound and carbonic anhydride, together with a small amount of other products. Succinic acid itself is not attacked by alkaline diazobenzene.

Difformazyl crystallises in greenish-brown plates, with a surface lustre which varies from yellow to dark green according to the conditions of crystallisation. It melts at 226° , gives a red powder, and forms deep red solutions in organic solvents. It is very readily soluble in benzene, readily in hot alcohol, almost insoluble in light petroleum. With sulphuric acid, it yields a deep, indigo-blue solution. It is a strong base, forming salts which are readily soluble in water, but almost insoluble in dilute acids, so that they are precipitated from aqueous solution by the addition of a few drops of acid. The *sulphate*, $C_{22}H_{22}N_8 \cdot H_2SO_4$, forms dark, orange-red needles with a splendid golden-green reflection, and decomposes at 232° ; it crystallises well from alcohol and chloroform, in which it is readily soluble. The *hydrochloride*, $C_{22}H_{22}N_8 \cdot HCl$, is very similar to the sulphate; it decomposes at 248° . When treated with alcoholic ammonium sulphide, *difformazyl* is converted into diamidrazone, $N_2HPh \cdot C(NH_2) \cdot C(NH_2) \cdot N_2HPh$, identical with that obtained by Senf from phenylhydrazine and cyanogen. This mode of formation is a further proof of the formula proposed for diamidrazone by Bamberger and de Gruyter (this vol., i, 23). A. H.

Aromatic Oxychlorophosphines. By A. MICHAELIS and G. SCHULZE (*Ber.*, 26, 1937–2940).—When phosphorus oxychloride and dry aniline hydrochloride are heated together in molecular proportions, together with a little benzene, hydrogen chloride is evolved, and *anilineoxychlorophosphine*, $NHPh \cdot POCl_2$, is formed. The latter is separated from the oily residue by treatment with light petroleum, and it can be purified by recrystallisation from benzene and light petroleum. It forms thick, almost cubic, crystals or needles, melts at 84° , and does not fume in the air; it cannot be distilled without decomposition, and is slowly attacked by cold water, readily by the hot liquid. With alcohols, it forms ethereal salts which are being investigated. *Paratoluidineoxychlorophosphine*, $C_6H_4Me \cdot NH \cdot POCl_2$, is obtained in a similar manner from paratoluidine, and forms thick, white crystals melting at 104° . H. G. C.

Thioaldehydes and their Conversion into Derivatives of Stilbene. By K. KOPP (*Annalen*, 277, 339–361; compare Abstr., 1892, 718).— β -*Trithiosalicylaldehyde*, $C_{11}H_8S_3O_2$, is prepared by dissolving salicylaldehyde in a well cooled alcoholic solution of hydrogen chloride, treating with hydrogen sulphide for 2–2½ hours at -10° , and allowing the product to remain for two days; too large a quantity of hydrogen chloride is to be avoided. The compound separates from alcohol in six-sided plates containing 3 mols. C_2H_5O , and, when pure, is colourless and tasteless; it melts at 210° . When iodine is added to its alcoholic solution, the compound remains unaltered; inasmuch, therefore, as all the known α -trithioaldehydes are by this treatment converted into the β -modifications (Baumann and Fromm, Abstr., 1891, 1050), the author's conclusion that his substance is the β -compound

appears justified. The sodium derivative, $C_{21}H_{15}S_2O_2Na_3$, crystallises in faintly yellowish leaflets; the benzoyl derivative, $C_{42}H_{30}S_2O_4$, melts at 218° . Polymerised benzoylthiosalicylaldehyde is obtained by the action of hydrogen sulphide on a 10 per cent. solution of benzoylthiosalicylaldehyde in alcohol; the compound melts at $95-98^\circ$, and is converted into benzoyl- β -trithiosalicylaldehyde when dissolved in ethylic iodide and heated with iodine.

β -Trithiomethahydroxybenzaldehyde, $C_{21}H_{15}S_3O_2$, prepared from methahydroxybenzaldehyde in the same manner as the isomeride, forms colourless needles containing 3 mols. C_2H_5O , and melts at 212° ; the benzoyl derivative melts at 146° . Polymerised thiomethylmethahydroxybenzaldehyde is obtained when an alcoholic solution of methylmethahydroxybenzaldehyde is saturated with hydrogen sulphide, and allowed to remain for 1-2 days; it sinters at 90° , and melts at $95-97^\circ$. If heated at 160° , or treated with iodine in ethylic iodide solution, β -trithiomethylmethahydroxybenzaldehyde, $C_{24}H_{18}S_3O_2$, is produced; it melts at 147° , and becomes brown at 180° .

β -Trithioparahydroxybenzaldehyde, $C_{21}H_{15}S_3O_2$, commences to darken at 165° , and melts at 215° ; the tribenzoyl derivative melts at 225° .

Benzoylparahydroxybenzaldehyde, $OBz \cdot C_6H_4 \cdot CHO$, melts at 72° , and is converted by hydrogen sulphide into a polymeric benzoylthioparahydroxybenzaldehyde melting at 98° , which yields the β -trithio-modification when treated with iodine.

β -Dihydroxystilbene, $OH \cdot C_6H_4 \cdot CH:CH \cdot C_6H_4 \cdot OH$ [$OH:OH = 2:2'$], is obtained in small amount on heating β -trithiosalicylaldehyde or the polymeric compound, but more conveniently by warming dibenzoyloxystilbene (see below) with alcoholic potash; it crystallises from alcohol in transparent, flat needles having a bluish fluorescence, and melts at 197° . If distilled, it undergoes partial decomposition; the main portion, however, passes over unaltered, whilst a small quantity is converted into α -dihydroxystilbene, m. p. 95° (Harries, Abstr., 1892, 168); the two compounds are separated by taking advantage of the fact that the lower melting isomeride is more volatile with steam than the higher. The conversion of the latter into the former was not accomplished. Attempts to convert stilbene into an isomeride by heating it were unsuccessful. Elbs (Abstr., 1893, i, 272) has observed the existence of two diethoxydinaphthostilbenes, which appear, however, to have different relations to each other from what the dihydroxystilbenes have. β -Dibenzoyloxystilbene, $C_{26}H_{20}O_4$, already mentioned, is obtained when a small portion of β -trithiobenzoylsalicylaldehyde is rapidly raised to a temperature of $295-305^\circ$; it forms colourless needles, melts at 174° , and the dibromide melts at 176° with decomposition. Harries describes an isomeric compound (*loc. cit.*).

Diorthomethoxystilbene (see Abstr., 1892, 719).

Dimethoxystilbene, $OMe \cdot C_6H_4 \cdot CH:CH \cdot C_6H_4 \cdot OMe$ [$OMe:OMe = 3:3'$], is obtained by distilling polymerised methylthiomethahydroxybenzaldehyde with a large excess of iron powder; it crystallises in rhombic tables, and melts at $99-100^\circ$. Dibenzoyloxystilbene is formed when β -trithiobenzoylmetahydroxybenzaldehyde is heated at 300° ; it melts at 160° .

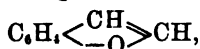
Paradihydroxystilbene (Elbs and Hoermann, Abstr., 1889, 997) is

obtained in small quantity by heating trithiohydroxybenzaldehyde, or in better yield by hydrolysing its dibenzoyl derivative with alcoholic potash. The last mentioned *dibenzoyl* derivative is formed when polymerised benzoylthioparahydroxybenzaldehyde is heated at $210-220^{\circ}$; it melts at 238° . A stilbene derivative is not obtained when polymerised benzoylthioparahydroxybenzaldehyde is rapidly heated to 250° .

Diparamethoxystilbene (see Abstr., 1892, 719; 1893, i, 272).

A. R. L.

New Synthesis of Coumarone. By G. KOMPPA (*Ber.*, 26, 2968—2972).—Coumarone was first obtained by Fittig and Ebert (*Annalen*, 226, 354), who assigned to it the formula



but did not strictly prove its constitution. The accuracy of this formula is proved by the author, who has prepared coumarone synthetically from orthamido-*w*-chlorocinnamene, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CHCl}$. This substance has been previously obtained by Lipp (*Ber.*, 17, 1070), but was not further investigated by him. It crystallises from light petroleum in long prisms melting at $55.5-56.5^{\circ}$, and separates from alcohol in well-formed, monosymmetric crystals. The *platinochloride* forms long, brownish-yellow needles. *Acetylorthamido-w-chlorocinnamene*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CHCl}$, crystallises in dazzling white, matted needles, melting at $158-159^{\circ}$, and is readily soluble in alcohol. *Orthohydroxy-w-chlorocinnamene*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CHCl}$, is obtained by the action of nitrous acid on the amido-compound. It crystallises in long, thick needles melting at $54.5-55.5^{\circ}$, and is readily soluble in alcohol, &c., sparingly in water. It may be preserved for a considerable time in the air without change.

When this hydroxy-compound is dissolved in concentrated aqueous potash, and the solution heated by steam, it is converted, with elimination of hydrogen chloride, into coumarone, which separates as an oil.

The author is endeavouring to prepare the hitherto unknown benzothiophen in a similar manner.

A. H.

Some Derivatives of Methylic Gallate and Dibromogallate. By A. BIÉTRIX (*Bull. Soc. Chim.*, [3], 9, 692—696).—The bismuth derivative of methylic gallate, $\text{COOMe} \cdot \text{C}_6\text{H}_4(\text{OH})_2 \cdot \text{O} \cdot \text{Bi}(\text{OH})_2$, is a clear yellow powder, insoluble in water, alcohol, and ether. It is decomposed on melting. The lead derivative, whatever the proportion of lead acetate used to precipitate it, has a nearly constant composition, its formula being



It is a white precipitate, insoluble in water, alcohol, and ether, and blackens on heating.

Methylic lead dibromogallate, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Br}_2(\text{O}_2\text{Pb}) \cdot \text{COOMe}$, is precipitated of a greenish-blue colour, rapidly becoming green. It is insoluble in all neutral solvents, and melts with decomposition.

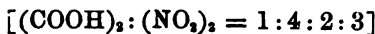
Methylic triacetyldibromogallate, $C_6Br_2(OAc)_3 \cdot COOMe$, is formed by heating together acetic chloride and methylic dibromogallate. It is a white compound melting at 150° , insoluble in water, and can be crystallised from boiling alcohol. W. T.

Iodoterephthalic acid and Iodosoterephthalic acid. By H. ABBS (*Ber.*, 26, 2951—2956).—*Iodoterephthalic acid*, $C_6H_3I(COOH)_2$, is readily prepared by the action of alkaline permanganate on met-iodoparatoluic acid (*Abstr.*, 1893, i, 581), and crystallises from hot water in slender, yellow needles, which in the crude state melt at 274 — 276° , but sublime when pure. The neutral *sodium*, *barium*, and *calcium* salts are crystalline and soluble in water, whilst the *silver* salt forms an amorphous, white, insoluble powder. The *dimethylic* salt crystallises from hot water in long, yellowish needles, melts at 77 — 78° , has an aromatic odour and sharp taste; the *monomethylic* salt melts at 186° .

Iodoterephthalic acid is converted by the action of fuming nitric acid or of an excess of potassium permanganate into the corresponding *iodosoterephthalic acid*, $IO \cdot C_6H_3(COOH)_2$, which forms a yellowish precipitate, melts at 260° with evolution of gas, and liberates iodine from potassium iodide solution. It may also be obtained by converting iodoterephthalic acid into the iodochloride, which is a yellow, wax-like mass, and acting on it with a little soda solution. The iodoso-acid only yields salts in which one atom of hydrogen is displaced by metals, the acid *sodium*, *ammonium*, *barium*, and *calcium* salts being crystalline, and the *silver* salt a yellow, amorphous mass. The *monomethylic* salt crystallises in white, lustrous plates, and decomposes potassium iodide in the cold. The fact that the iodoso-acid only acts as a monobasic acid, whilst the iodo-acid is bibasic, points to the conclusion that an intramolecular salt formation has taken place in the iodosoterephthalic acid, which may, like iodosobenzoic acid, be represented by the tautomeric formulæ
$$\begin{array}{c} O-CO \\ | \\ HO-I-C_6H_3-COOH \end{array}$$
 and $IO \cdot C_6H_3(COOH)_2$.

All attempts to replace the amido-group in amidometatoluic acid by iodine were unsuccessful, the corresponding hydroxy-acid being always obtained, whatever method was employed. H. G. C.

Dinitroterephthalic acids. By C. HÄUSSERMANN and E. MARTZ (*Ber.*, 26, 2982—2985).—*Orthodinitroterephthalic acid*



is prepared by heating dinitroparaxylene m. p. 93° , or dinitroparatoluylic acid m. p. 248° , with nitric acid of sp. gr. 1.5 at 170° . It is only slightly soluble in nitric acid, and separates from hot water in well-formed crystals with a vitreous lustre. It melts with decomposition at above 290° , and deflagrates when rapidly heated on platinum foil.

Metadinitroterephthalic acid $[(NO_2)_2 = 3 : 5]$ may be obtained from the dinitroparaxylene m. p. 124° , or from the dinitroparatoluylic

acid m. p. 158° , by oxidation with nitric acid and by the nitration of mononitroterephthalic acid. It dissolves readily in hot water, forming a yellow solution, and separates on cooling in yellowish, distorted crystals, with a vitreous lustre, which melt at 255° with decomposition. The *barium salt* is a pale yellow, flocculent mass, and is readily soluble in water. Separation of barium carbonate takes place when the solution is boiled; and the salt completely decomposes into barium carbonate and 1:3:5-dinitrobenzoic acid, when the solution is heated for some time at $200-250^{\circ}$.

The *diethylic salt* forms white, matted needles, which melt at 197° and volatilise with decomposition at a higher temperature. It is readily soluble in alcohol, sparingly in water.

Paradinitroterephthalic acid $[(NO_2)_2 = 2:5]$ is formed by the oxidation of the dinitroparaxylene m. p. $147-148^{\circ}$, but is best prepared from the paradinitroparatoluic acid m. p. 194° . It separates from water in small, prismatic crystals with a vitreous lustre, and dissolves readily in hot water, forming an almost colourless solution. It melts above 280° with vigorous evolution of gas, and deflagrates when heated on platinum foil. The *barium salt* is a flesh-coloured powder which is readily soluble in water. The *diethylic salt*, which is rather less soluble in alcohol, ether, and benzene than the corresponding meta-compound, crystallises in lustrous needles, and melts at 144° ; when treated in alcoholic solution with tin and hydrochloric acid, it is converted into diethylic diamidoterephthalate, which was obtained by Baeyer (*Ber.*, 19, 430) by the oxidation of the diimide of ethylic succinosuccinate.

A. H.

Sulphones from Benzylic Alcohol and Benzoic acid. By P. GENVRESSE (*Bull. Soc. Chim.*, [3], 9, 707-710).—*Dibromditolylsulphone*, $SO_2(C_6H_4 \cdot CH_2Br)_2$, is obtained by brominating ditolylsulphone. It forms small, white crystals, melts at 108° , and is soluble in hot alcohol and in chloroform.

Dihydroxyditolylsulphone, $SO_2(C_6H_4 \cdot CH_2OH)_2$, is obtained by treating the preceding compound with aqueous potassium carbonate. It forms a mass of fine needles. It is soluble in alcohol and in boiling water, much less soluble in cold water. It melts at 156° , and decomposes on further heating.

Dicarboxydiphenylsulphone, $SO_2(C_6H_4 \cdot COOH)_2$, is obtained by treating the preceding bromo-compound with potassium permanganate in alkaline solution. It is a white, crystalline substance, and, though insoluble in water and almost insoluble in alcohol, is very soluble in dilute alkaline solutions. Its silver salt is obtained as a white precipitate, not blackening in the light. A pale green copper salt has also been obtained, but has not yet been analysed. W. T.

Action of Sulphuryl Chloride on Aromatic Hydrocarbons. By A. TÖHL and O. EBERHARD (*Ber.*, 26, 2940-2945).—Sulphuryl chloride acts on benzene with formation simply of monochlorobenzene, but if aluminium chloride is added to the mixture, a considerable quantity of benzenesulphonic chloride and a small amount of diphenylsulphone are also obtained. Toluene is chlorinated by

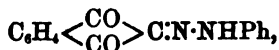
sulphuryl chloride both in the benzene nucleus and the side chain, but in presence of aluminium chloride the chief product is paratoluenesulphonic chloride, small quantities of parachlorotoluene and paradi-tolylsulphone being also obtained. Metaxylene and paraxylene behave in a similar manner to toluene, the latter yielding *diparaxylsulphone*, which crystallises in needles. Mesitylene is attacked by sulphuryl chloride at the ordinary temperature; if, however, the mixture be kept cool, and aluminium chloride then added, chloromesitylene and mesitylenesulphonic chloride are formed. Pseudocumene behaves in a similar manner, but durene, prehnitine, and pentamethylbenzene yield only chlorinated products. Ethylbenzene is converted into parachlorethylbenzene, parethylbenzenesulphonic chloride, and *ethylbenzenesulphone*; the latter crystallises in transparent plates, and melts at 102°. Isopropylbenzene yields the corresponding products, the *isopropylbenzenesulphone* melting at 109–110°. Cymene yields only resinous products, whilst naphthalene is converted chiefly into α -chloronaphthalene and a small quantity of α -naphthalenesulphonic chloride.

H. G. C.

The Strength of Orthosulphobenzoic acid. By J. SHIELDS (*Ber.*, 26, 3027–3028).—The author points out that the formation of ammonium orthosulphobenzoate by heating orthosulphobenzoic acid with ammonium chloride in concentrated solution simply proves that this acid is less volatile than hydrochloric acid, but not that it is a stronger acid, as stated by Jesurun (*Abstr.*, 1893, i, 715). A determination of the relative strength of the acids must necessarily take into account the law of mass action.

J. B. T.

Diketohydrindene. By W. WISLICENUS and F. REITZENSTEIN (*Annalen*, 277, 362–374).—*Triketohydrindene- β -hydrazone*,



is precipitated when diketohydrindene is dissolved in the smallest possible quantity of dilute soda and a solution of diazobenzene chloride together with sodium acetate added; it crystallises from aqueous alcohol in orange-yellow, prismatic needles, melts at 190°, and dissolves in concentrated sulphuric acid with a red colour, which remains unchanged on adding a drop of ferric chloride solution, but changes first to blue and subsequently to reddish-violet on the addition of potassium dichromate. When ether is added to its solution in alcoholic soda, the sodium salt separates as a reddish-yellow precipitate.

When an alcoholic solution of benzylidenediketohydrindene (*Annalen*, 252, 75) is treated with phenylhydrazine, benzaldehydphenylhydrazone is obtained, together with the mono- and di-hydrazone of diketohydrindene.

It has been shown (*Annalen*, 252, 72) that when diketohydrindene is heated by itself or boiled with water, a condensation product, anhydroidiketohydrindene, $\text{C}_{12}\text{H}_{10}\text{O}_2$, is formed; the authors have confirmed this formula by the cryoscopic method, and the following experiments render it probable that the compound has the constitution

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$C_6H_4 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C:C < \begin{smallmatrix} C_6H_4 \\ CH_2 \end{smallmatrix} > CO$. It dissolves in sodium hydroxide solution with an intense red colour, which differs from that exhibited by phenolphthalein in that the colour is not destroyed by excess of alkali. When the alkaline solution is evaporated, the residue taken up with alcohol, the alcoholic solution evaporated, and the residue triturated with alcohol, the *sodium* salt, $C_{18}H_8O_2Na$, is obtained as a dark, brownish-red powder; the *calcium* salt, $(C_{18}H_8O_2)_2Ca$, is a bluish-black precipitate; and the *copper* salt an almost black precipitate. The *oxime*, $C_{18}H_{10}O_2 \cdot NOH$, crystallises in small, yellow needles, commences to darken at 210° , and decomposes above this temperature without previously melting; whilst its *acetyl* derivative forms yellow leaflets, and decomposes above 180° . When anhydrosidiketohydrindene is suspended in absolute alcohol, and phenylhydrazine (4 mols.) added, diketohydrindenodiphenylhydrazone, $C_6H_4 < \begin{smallmatrix} C(N_2HPh) \\ C(N_2HPh) \end{smallmatrix} > CH_2$ (m. p. $171-172^\circ$) is obtained; but if less phenylhydrazine (1 mol.) is used, diketohydrindenomonophenylhydrazone is formed. When anhydrosidiketohydrindene is treated with concentrated sulphuric acid at the ordinary temperature, or with acetic anhydride at $150-160^\circ$, further condensation takes place, and a red compound, $(C_{18}H_8O_2)_n$, which does not melt at 310° , is produced. A. R. L.

Symmetrical β -Diketones of the Aromatic Series. By A. BÉHAL and V. AUGER (*Bull. Soc. Chim.*, [3], 9, 696—704).—Malonic chloride reacts with aromatic hydrocarbons in presence of aluminium chloride to give a diketone of the type $R \cdot CO \cdot CH_2 \cdot CO \cdot R$, a ketone of the type $R \cdot CO \cdot Me$, and a hydrocarbon. The diketones act as acids, forming metallic derivatives. They are crystalline substances, insoluble in water, but soluble in aqueous solutions of alkalis and in organic solvents. Their stability appears to increase with the number of carbon atoms in the molecule; the lower members of the series, such as dibenzoylmethane, are readily decomposed by alkalis into ketones and acids.

Ditoluylmethane, $CH_2(CO \cdot C_6H_4Me)_2$, [$Me : CO = 1 : 4$], is prepared by the action of malonic chloride on toluene. It melts at 126° . It is very soluble in benzene but only sparingly so in absolute alcohol, from which it is deposited in long needles; its alcoholic solution becomes violet on adding ferric chloride, and on diluting with water, a red, crystalline powder of the ferric salt is deposited. It is decomposed by concentrated soda into paramethylbenzoic acid and methylphenyl methyl ketone.

Diethylbenzoylmethane, $CH_2(CO \cdot C_6H_4Et)_2$, [$Et : CO = 1 : 4$], resembles the above in mode of preparation and in properties. It melts at 42° . When decomposed by soda, it yields parethylbenzoic acid and ethylphenyl methyl ketone; the latter has a sp. gr. 0.9719 and an odour of aniseed. The hydrocarbon produced along with this diketone is metadiethylbenzene (compare *Abstr.*, 1890, 493).

Diortho-xylolmethane, $CH_2(CO \cdot C_6H_3Me)_2$, [$Me : CO = 1 : 2 : 4$], melts at 138° . It is attacked by soda with difficulty, and resembles

the preceding compounds in its products of decomposition and properties. It gives a brown coloration with ferric chloride.

Dimetaxyloymethane [$\text{Me}_2 : \text{CO} = 1 : 3 : 4$] is very soluble in acetic acid or alcohol. It forms prisms melting at 82° . With ferric chloride, it gives a red coloration, becoming more violet on the addition of water. In its properties and mode of decomposition by soda, it resembles the foregoing compounds.

Diparazyloymethane [$\text{Me}_3 : \text{CO} = 1 : 4 : 3$], boils in a vacuum at about 250° . It is very soluble in benzene and light petroleum, but only sparingly in 95 per cent. alcohol. It forms small crystals melting at $101\text{--}102^\circ$. With very concentrated soda, it produces the corresponding dimethylbenzoic acid and dimethylphenyl methyl ketone [$\text{Me}_3 : \text{CO} = 1 : 4 : 3$], boiling at 225° under 764 mm. pressure, and having a sp. gr. = 1.0154 at 0° .

Dimeritoylmethane, $\text{CH}_2(\text{CO} \cdot \text{C}_6\text{H}_4\text{Me}_3)_2$ [$\text{Me}_3 : \text{CO} = 1 : 3 : 5 : 2$], melts at $96\text{--}97^\circ$. It requires to be heated at 300° in a sealed tube with soda, and then yields a trimethylphenyl methyl ketone and isodurylic acid. It gives a red coloration with ferric chloride in alcoholic solution.

A diketone from cymene has been obtained as an impure liquid. With soda, in a sealed tube at 300° , it gave, in addition to an acid which was not examined further, a ketone of agreeable odour, boiling at 240° , and yielding an oxime boiling at 176° (21 mm.) and melting at 84° . No diketone has been obtained in a pure state from naphthalene by means of this reaction.

W. T.

Physical Modification of β -Carbodiphenylimide and β -Carbodiparatolylimide. By C. SCHALL (*Ber.*, 26, 3064—3065).—When β -carbodiphenylimide is carefully heated to its melting point and then suddenly and strongly cooled, it solidifies to a yellowish, amorphous mass, which melts at a lower temperature and is more soluble than the β -modification. When slowly heated, it melts at $96\text{--}99^\circ$, and at $108\text{--}130^\circ$ is reconverted into the β -modification melting at $158\text{--}160^\circ$.

β -Carbodiparatolylimide, when heated and cooled in the same way, is at first semi-fluid, but after a time solidifies. It now melts at $60\text{--}70^\circ$, and cannot be reconverted into the β -modification by further heating.

Triparatolyguanidine, when heated and quickly cooled, melts at $46\text{--}50^\circ$, and at $70\text{--}80^\circ$ is reconverted into the ordinary modification, melting at $123\text{--}124^\circ$.

A similar behaviour is shown by the compound obtained from β -carbodiphenylimide and phenylhydrazine. The new modification is always amorphous, even if the primary compound is crystalline and pure.

E. C. R.

Two Recent Publications on the Benzileoximes. By G. MINUNNI and G. ORTOLEVA (*Gazzetta*, 23, ii, 244—248).—This paper deals with the criticisms of Auwers and Siegfeld (*Abstr.*, 1893, i, 354) and of Claus (*Abstr.*, 1893, i, 355) on the authors' work (*Abstr.*, 1893, i, 97).

W. J. P.

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Reduction Products of Benzilehydrazone. By A. PUGOTTI (*Gazzetta*, 23, ii, 225—231).—In a previous preliminary note (*Abstr.*, 1893, i, 354), the author described a new base, obtained by reducing benzilehydrazone; the supposition that the base is amidodibenzile is now confirmed. Small quantities of aniline and dibenzile are also produced.

Amidodibenzile, $\text{CH}_3\text{Ph}\cdot\text{CHPh}\cdot\text{NH}_2$, is an oil having an aromatic odour, and boiling without appreciable decomposition at $310\text{--}311^\circ$ under 750 mm. pressure. It is very soluble in alcohol, ether, chloroform, or carbon bisulphide, but only sparingly in water. Its *hydrochloride* crystallises in small, white needles melting at $242\text{--}243^\circ$, and the *platinochloride* in golden scales which melt at about 188° . The *oxalate* is obtained as a white, crystalline precipitate melting at 158° ; the *picrate* melts at 190° .

The constitution of the base is established by the fact that on treating the hydrochloride with silver nitrite, phenylbenzylcarbinol is obtained.

Diphenylethyloxamide, $(\text{CH}_3\text{Ph}\cdot\text{CHPh}\cdot\text{NH})_2\text{C}_2\text{O}_2$, is prepared by heating the base on the water bath with an ethereal solution of ethylic oxalate. It forms white needles melting at 212° , and is soluble in chloroform or boiling benzene, but sparingly so in ether, alcohol, or water.

Acetamidodibenzile, $\text{CH}_3\text{Ph}\cdot\text{CHPh}\cdot\text{NHAc}$, obtained by heating amidodibenzile hydrochloride with acetic anhydride and fused sodium acetate, crystallises in white needles melting at $147\text{--}148^\circ$.

Dibenzilecarbamide, $\text{CH}_3\text{Ph}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is prepared by the action of potassium cyanate on the hydrochloride described above; it forms small, white crystals which melt at 98° , and is soluble in alcohol, ether, benzene, or chloroform. W. J. P.

Action of β -Naphthol and α - and β -Naphthylamines on the Nitrobenzaldehydes. By M. ZENONI (*Gazzetta*, 23, ii, 215—224).—The behaviour of β -naphthol towards aliphatic aldehydes has been studied by Hosaeus and by Abel (*Abstr.*, 1893, i, 100, 172); the present paper gives the results obtained with the nitrobenzaldehydes.

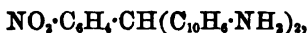
On adding a little sulphuric acid to an acetic acid solution of orthonitrobenzaldehyde and β -naphthol, *orthonitrobenzal- β -dinaphtholmethane*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_{10}\text{H}_7\cdot\text{OH})_2$, is slowly deposited; it forms a crystalline mass melting at 207° , is soluble in ether, chloroform, or acetone, but insoluble in benzene and in light petroleum. The corresponding *oxide*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}<\text{C}_{10}\text{H}_7>\text{O}$, is obtained by boiling the acid solution during the preparation of the previous substance. It forms beautiful, pale green, acicular crystals which turn brown above 250° ; it is sparingly soluble in the ordinary solvents.

Metanitrobenzal- β -dinaphtholmethane is prepared in a similar manner to its ortho-isomeride; it melts at 184° , and, on boiling with potash, yields an unstable substance which crystallises in beautiful golden scales. The dinaphthol derivative yields a crystalline *diacetyl* derivative which melts at 242° , and is very sparingly soluble in the ordin-

ary solvents. The *oxide* is obtained in silvery white scales melting at 220°.

Orthonitrobenzal- β -dinaphtholmethane could not be prepared, the *oxide* being obtained instead; this substance forms small, yellow needles which turn brown when heated above 260°.

On mixing acetic acid solutions of α -naphthylamine and metanitrobenzaldehyde, *metanitrobenzal- α -dinaphthylamine*,



separates. It is very soluble in ether or chloroform, and forms yellow laminae melting at 102—103°. The isomeric *para*-derivative is obtained in yellow needles melting at 161—162°, and the *ortho*-isomeride melts at 119—120°. The *meta*-derivative, obtained from β -naphthylamine, forms yellow crystals melting at 90—91°; the *para*-isomeride is obtained in yellow needles melting at 120—121°, whilst the *ortho*-derivative forms yellow crystals melting at 92—93°, and is very sensitive to light. These derivatives of the naphthylamines may also be prepared by boiling the alcoholic solutions of the two constituents. If, however, fuming hydrochloric acid is added to the alcoholic solutions before boiling, *nitrophenylhydronaphthacridines* are obtained; these will be subsequently studied. W. J. P.

A Naphthylene Diazosulphide. By P. JACOBSON and C. SCHWARZ (*Annalen*, 277, 257—261; compare this vol., i, 123).—It has been stated (*Abstr.*, 1888, 1307) that 2 : 1-ethenylamidonaphthyl mercaptan melts at 81°. The authors find that the melting point of the compound is not sharp, and, even after repeated recrystallisation from aqueous alcohol, it softens at 68—70°, and melts at about 80°; if, however, the crystals are kept over concentrated sulphuric acid in a partial vacuum, they effloresce and then melt sharply at 48°. When the compound is heated with phthalic anhydride and zinc chloride, a *phthalone* melting above 300° is formed. When the ethenyl base is heated at 220—230° with aqueous potash, the product dissolved in water, sodium nitrite added, and the solution treated in the cold with dilute sulphuric acid, *naphthylene diazosulphide*, $\text{C}_{10}\text{H}_6 \langle \text{N} \rangle \text{N}$ [$\text{N} : \text{S} = 1 : 2$], is obtained; it crystallises in small needles, having a bronzy lustre, melts at 89°, appears to decompose on exposure to light, and resembles phenylene diazosulphide in its behaviour.

A. R. L.

β -Naphtholcarboxylic acid (m. p. 216°) and its Derivatives. By S. ROBERTSON (*J. pr. Chem.*, [2], 48, 534—536).— β -Naphtholcarboxylic acid (m. p. 216°) was prepared by heating sodium β -naphthoxide with liquid carbonic anhydride at 270—280° in an autoclave. The product is converted into the ammonium salt, and then, by the action of phosphorus pentachloride, into the chloride, which, by treatment with boiling water, is converted into the pure acid. When treated with nitric acid, it yields, according to the conditions of working, either a mononitro or dinitro acid.

The *mononitro-acid*, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6(\text{OH}) \cdot \text{COOH}$, crystallises in lustrous, golden-yellow prisms, melts at 233—238° with decomposition, and,

when boiled with water, decomposes with evolution of carbonic anhydride. The *sodium, ammonium, and potassium salts* are described; they are anhydrous, and give insoluble microcrystalline precipitates with salts of the heavy metals. The *ethylic salt* crystallises in lustrous, greenish needles, melts at 160° , and is easily hydrolysed by cold alkalis.

Amido- β -naphtholcarboxylic acid crystallises in colourless, lustrous needles, decomposes before melting with the formation of a red dye, and yields dihydroxynaphthalenecarboxylic acid when boiled with acids. The *hydrochloride* crystallises in white, lustrous needles, and is hydrolysed by water or alcohol. *Diazonaphtholcarboxylic acid*,

$\text{OH}\cdot\text{C}_{10}\text{H}_7\langle\text{COO}\rangle^{\text{N}}\text{N}$, crystallises in long, brownish-yellow needles.

Chloronaphtholcarboxylic acid melts at 230° . *Dihydroxynaphthalene-carboxylic acid*, obtained by decomposing the diazo-compound with sulphuric acid, crystallises in long, greenish needles.

Dinitronaphtholcarboxylic acid crystallises in bright yellow, lustrous needles, melts at 252° with decomposition, but begins to decompose at 242° . The *ethylic salt* crystallises in white, prismatic needles, and melts at 198° .

E. C. R.

β -Naphtholcarboxylic acid (m. p. 216°). By R. MÖHLAU (*Ber.*, 26, 3065—3067; compare also S. v. Kostanecki, this vol., i, 91).—Naphthaleneazo- β -hydroxynaphthoic acid, obtained by the action of diazonaphthalene chloride on β -naphtholcarboxylic acid (m. p. 216°), yields, on reduction, amido- β -hydroxynaphthoic acid. The latter is converted by boiling with dilute sulphuric acid into the same β -naphthoquinolcarboxylic acid as that which is obtained by the action of carbonic anhydride on sodium β -naphthoquinol; it crystallises in yellow leaflets, melts at 207° with decomposition, and gives a green coloration with ferric chloride.

β -Amidonaphthoic acid is obtained by heating the β -naphtholcarboxylic acid with aqueous ammonia at 260 — 280° . It crystallises in lustrous, yellow leaflets, melts at 211 — 212° , and yields phthalic acid when oxidised with potassium permanganate. The diazosulphate, $\text{COOH}\cdot\text{C}_{10}\text{H}_7\cdot\text{N}_2\cdot\text{HSO}_4$, when treated with copper powder in alcoholic solution, yields β -naphthoic acid, which melts at 181 — 182° .

These reactions prove that the β -naphtholcarboxylic acid melting at 216° is the 2:3-compound.

E. C. R.

Relative Stability of certain Sulphonic Derivatives of Naphthalene. By P. FRIEDLAENDER and P. LUCHT (*Ber.*, 26, 3028—3034).—The authors have investigated the relative ease with which the sulphonic group of a number of naphthalene derivatives is replaced by hydrogen; the naphthol derivatives were treated in dilute acid, the naphthylamine derivatives in dilute alkaline solution at ordinary temperatures with sodium amalgam. The following compounds are practically unaltered:— β -Naphthalenesulphonic acid, α -naphtholsulphonic acid 1:2, β -naphtholsulphonic acids 2:3' and 2:2'. The following are slowly changed:— α -Naphtholsulphonic acids 1:3 and 1:2'. α -Naphthalenesulphonic acid, α -naphtholsulph-

onic acids 1:4, 1:4', 1:1', and β -naphtholsulphonic acid 2:1', are all readily attacked by sodium amalgam. α -Naphtholdisulphonic acids 1:2:4 and 1:4:2' are converted into sulphonic acids. α -Naphtholtrisulphonic acid 1:2:4:2' yields the disulphonic acid 1:2:2'. β -Naphtholdisulphonic acids 2:3':1' and 2:3:1' are converted into the sulphonic acid 2:3'. The following naphthylamine-sulphonic acids are readily reduced:— α -Naphthylaminesulphonic acids 1:4, 1:4', 1:1', β -naphthylaminesulphonic acids 2:4' and 2:1'. α -Naphthylamine-*c*-disulphonic acid 1:3:1' is rapidly converted into the 1:3-acid. β -Naphthylaminedisulphonic acid 2:4:1' yields β -naphthylamine. The α -sulphonic acids 1:2, 1:3, 1:2', and the β -acids 2:3' and 2:2' are much more stable.

2:3'-Naphthylenediamine is prepared by the reduction of the nitro-sulphonic acid from 2:1'- β -naphthylaminesulphonic acid, and subsequent elimination of the sulphonic group; it crystallises from water in colourless plates, darkens in air, and melts at 216°. With ferric chloride, a green coloration is obtained, which becomes blue on warming. Chromic anhydride, bromine water, and calcium hypochlorite all produce a dark green coloration which changes to brown. The *diacetyl derivative* is crystalline. The original acid, therefore, has the constitution $[\text{NH}_2 : \text{SO}_3\text{H} : \text{NO}_2 = 2 : 1' : 3']$. In a similar manner it is shown that the naphthylenediaminesulphonic acid from α -naphthylaminedisulphonic acid 1:4:3' yields 1:3'-naphthylenediamine, and that its constitution is $[\text{NH}_2 : \text{SO}_3\text{H} : \text{NH}_2 = 1 : 4 : 3']$. 1:3'-Dihydroxynaphthalene-4-sulphonic acid and 3':1-amidonaphthol-4-sulphonic acid yield respectively 1:3'-dihydroxynaphthalene and an amidonaphthol, which has not yet been described. The following β -sulphonic acids are not decomposed by sodium amalgam:—1:1'-Dihydroxynaphthalene-3:3'-disulphonic acid, 2:3-dihydroxynaphthalene-3'-sulphonic acid, 1:1'-diamidonaphthalene-3:3'-disulphonic acid, and 2:1'-amidonaphthol-3'-sulphonic acid. α -Sulphonic acids are, therefore, much more easily and completely reduced at ordinary temperatures than β -sulphonic acids.

J. B. T.

Dihydroanthrol and Dihydroanthramine. By E. BAMBERGER and F. HOFFMANN (*Ber.*, 26, 3068—3072).—In accordance with Bamberger's centric hypothesis, anthrol and anthramine are capable of taking up only two hydrogen atoms, and these combine with the central carbon atoms and the six-carbon atom rings become benzene rings. The properties of dihydroanthrol and dihydroanthramine are in accordance with this hypothesis; they show the typical properties of phenol and aniline respectively.

Dihydroanthrol, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ < \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_3\text{OH}$, is obtained by reducing anthrol with sodium and absolute alcohol. A small quantity of anthracene dihydride which is formed is separated by steam distillation, and the filtered solution is then precipitated with acid. It crystallises in white, lustrous plates, melts at 129.5°, and dissolves in sodium hydroxide with a yellow coloration and green fluorescence. It gives a yellow solution with concentrated sulphuric acid, which, on heating, turns greenish-yellow and then violet. It yields a raspberry-

red dye with diazosulphanilic acid. It sublimes, when heated at 200° , in a current of carbonic anhydride, and is slowly volatile with steam. Unlike anthrol, it is not altered by boiling with alcohol and hydrochloric acid, or by heating with ammonia or with acetamide. The *acetyl compound* is a yellow, crystalline powder, melts at 148° , and dissolves in alcohol with a blue fluorescence. It gives a golden-yellow solution with concentrated sulphuric acid, which, on heating, turns green and then dark violet. The *benzoyl compound* crystallises in bright yellow nodules, and melts at 124° . The *ethoxy-compound*, $C_6H_4 \cdot C_2H_4 \cdot C_6H_5 \cdot OEt$, obtained by warming dihydroanthrol with ethylic iodide, potassium hydroxide, and absolute alcohol, crystallises in white aggregates, and melts at 107° . Dihydroanthrol is not altered by boiling with amyl alcohol and sodium.

Dihydroanthramine, $C_6H_4 < \begin{smallmatrix} CH_3 \\ CH_2 \end{smallmatrix} > C_6H_5 \cdot NH_2$, has already been described by Liebermann and Bollert (*Ber.*, 15, 853). Unlike anthramine, which is intensely yellow and is a feeble base, it is colourless, and readily dissolves in very dilute acids. When treated with nitrous acid, it yields a *diazo-compound*, which gives intensely coloured dyes with aromatic bases and phenols, and when distilled with steam, is converted into dihydroanthrol. E. C. R.

Isomerism in the Terpene Series. By O. WALLACH (*Ber.*, 26, 3072—3077).—The author gives an explanation of the relations between limonene (or dipentene) derivatives and terpinol which accounts for the dihydrohalogen additive products of limonene being inactive, whilst some limonene hydrochlor-nitrolamines are active. An asymmetric carbon atom always occurs in the latter, and not in the former, on this interpretation. J. W.

Volatile Hydrocarbons in Essence of Valerian. By OLIVIERO (*Compt. rend.*, 117, 1096—1097).—That fraction of the volatile hydrocarbons from essence of valerian which boils at about 157° consists partly of a terebenthene and partly of a camphene, which can be separated by the action of alcoholic potassium acetate on the monhydrochlorides. This camphene is *laevogyrate* ($[\alpha]_D = -21^{\circ}$), and yields a monhydrochloride which is *dextrogyrate*.

The monhydrochloride of the terebenthene has a specific rotatory power $[\alpha]_D = -25^{\circ}$. The camphene and terebenthene are accompanied by a small quantity of a feebly *laevogyrate* citrene.

C. H. B.

Presence of Camphene in Oil of Spike. By G. BOUCHARDAT (*Compt. rend.*, 117, 1094—1096).—Oil of spike consists almost entirely of camphor, linalol, and a small quantity of borneol and its isomerides. but also contains a small quantity of a hydrocarbon, $C_{10}H_{16}$, which boils at 158 — 160° , and has all the properties of the camphenes. Its rotatory power is $+29^{\circ} 10'$, and it yields a monhydrochloride with a rotatory power of $-20^{\circ} 15'$. This hydrochloride is decomposed when heated with an alcoholic solution of potassium acetate, and the hydrocarbon itself, when heated at 100° with glacial formic acid, yields borneol formate, together with some diterpilene, which is probably

derived from a small quantity of terebenthene associated with the camphene.

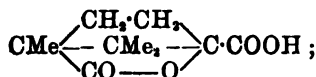
It is noteworthy that borneol and a camphene occur together, according to Oliviero, in essence of valerian, and are both lævogyrate, whilst in oil of spike they are both dextrogyrate. In both cases the camphene doubtless results from the decomposition of ethereal derivatives of borneol, either during the life of the plant or by simple distillation with water. C. H. B.

New Source of Rhodinol. By P. MONNET and P. BARBIER (*Compt. rend.*, 117, 1092—1094).—When oil of pelargonium is subjected to careful fractional distillation under reduced pressure, it yields *rhodinol*, $C_{10}H_{17}OH$, identical in all its physical and chemical properties with the rhodinol obtained from oil of roses; it boils at 124° under a pressure of 14 mm.; sp. gr. at $0^{\circ} = 0.8886$; refractive index $n_D = 1.4652$ and $n_D = 1.4789$ at 16.7° ; specific rotatory power $[\alpha]_D = -2^{\circ} 34'$. C. H. B.

Constitution of Camphor and its Derivatives. By J. BREDT (*Ber.*, 26, 3047—3057).—The products of the oxidation of camphor with nitric acid are camphoric acid, $C_{10}H_{16}O_4$, camphanic acid, $C_{10}H_{14}O_4$, and camphoronic acid, $C_9H_{14}O_4$. They form a graduated series: thus camphoronic acid is obtainable by the oxidation of camphoric and camphanic acids, and camphanic acid is formed by the oxidation of camphoric acid. Camphoronic acid is a tribasic acid, somewhat resembling tricarballic acid in its behaviour; when subjected to prolonged distillation it yields carbonic anhydride, water, carbon, isobutyric acid, trimethylsuccinic acid, and small quantities of bye-products resembling phorone. From these results the author assigns to camphoronic acid the constitution



and thence deduces the following constitutional formulæ: camphoric acid, $\begin{array}{c} CH_2 - CH_2 \\ | \quad | \\ COOH \cdot CMe \cdot CMe_2 \cdot CH \cdot COOH \end{array}$; camphanic acid,



camphor, $\begin{array}{c} CH_2 \cdot CH_2 \\ \diagup \quad \diagdown \\ CMe \quad CMe_2 \quad CH \\ \diagdown \quad \diagup \\ CO \cdot CH_2 \end{array}$. This formula correctly expresses the

reaction of camphor and its derivatives. Thus it explains the formation of bromocamphoric acid, and its conversion into camphanic acid; the production of dinitrocaproic acid by the prolonged action of nitric acid on camphor; the formation of cymene from camphor, and of isopropylsuccinic acid from camphoric acid, &c. The author gives constitutional formulæ explaining these reactions.

According to the author's formula, only two isomeric camphenes are possible, namely, $\begin{array}{c} CH_2 \cdot CH_2 \\ \diagup \quad \diagdown \\ CMe \quad CMe_2 \quad CH \\ \diagdown \quad \diagup \\ CH : CH \end{array}$ and $\begin{array}{c} CH_2 \cdot CH_2 \\ \diagup \quad \diagdown \\ CMe \quad CMe_2 \quad C \\ \diagdown \quad \diagup \\ CH_2 \cdot CH \end{array} = C$.

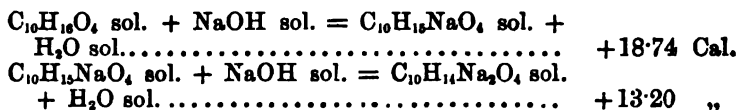
The second formula then expresses the constitution of pinene, and from this the constitution of terpin is expressed by the formula $\text{OH} \cdot \text{CMe} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C}(\text{OH}) \cdot \text{CHMe}_2$, which is the formula assigned to terpin by Wallach (Abstr., 1891, 1081) and v. Baeyer (*Ber.*, **26**, 2564). E. C. R.

Heat of Neutralisation of Camphoric acid. By G. MASSOL (*Bull. Soc. Chim.*, [3], **9**, 719—721).—Purified camphoric acid, m. p. 180° , has a solubility in water at 8° of 4.2 grams per litre; its solution is accompanied by absorption of heat: 1.87 Cal. (200 grams in 24 litres). The heat of neutralisation by soda is 27.16 Cal., 13.77 and 13.39 Cal. being developed for the first and second equivalents respectively (solid acid dissolved in soda solution).

Sodium hydrogen camphorate is not obtained by the spontaneous evaporation of its solution, but varying mixtures of normal and acid salts. The heat of solution of anhydrous sodium hydrogen camphorate (222 grams in 10 litres) is +4.37 Cal.

Normal sodium camphorate crystallises with $5\text{H}_2\text{O}$; the anhydrous salt is very soluble in water with development of heat, +15.77 Cal. (244 grams in 8 litres).

Heat of formation of the salts in the solid state—



The total heat of formation of the sodium salt, +31.94 Cal., is much less than with other bibasic organic acids; that of the acid salt is sensibly equal to the average heat of formation of the corresponding salts of the monobasic fatty acids. W. T.

Datiscin and its Decomposition Products. By E. SCHUNCK and L. MARCHLEWSKI (*Annalen*, **277**, 261—276).—Datiscin was prepared by extracting the bruised roots of *Datisca cannabina* with dilute alcohol, distilling off the alcohol, extracting the residue with water, treating the aqueous solution with a small quantity of lead acetate (basic?), and concentrating the filtrate, from which datiscin separates on cooling. It is repeatedly recrystallised from boiling water, when the crystals have but a faintly yellow tint. In its general properties, datiscin agrees with Stenhouse's description (*Annalen*, **98**, 167); it is very sparingly soluble in ether, and melts at 190° . Air-dried datiscin gave, on analysis, values agreeing with the formula $\text{C}_{21}\text{H}_{32}\text{O}_{11} + 2\text{H}_2\text{O}$, and that dried at 130° gave values agreeing with the formula $\text{C}_{21}\text{H}_{34}\text{O}_{11} + \text{H}_2\text{O}$. Specimens which had been dried at the latter temperature, however, were frequently found to have undergone decomposition.

When datiscin is boiled with dilute sulphuric acid, datiscetin separates from the solution on cooling, and a sugar, which is not glucose, as Stenhouse supposed, but rhamnose, remains dissolved. The rhamnose was identified by elementary analysis and by its melting

point (91°), as well as by means of its osazone and sodium compound.

Datiscetin, $C_{15}H_{13}O_6$, crystallises from alcohol in bright yellow needles, melts at 237° (uncorr.), and dissolves in concentrated sulphuric acid, forming a yellow solution, which subsequently exhibits a beautiful blue fluorescence. The above formula was confirmed by determinations of the molecular weight by the ebullioscopic method. The lead salt has the composition $C_{15}H_{10}O_6Pb$. When datiscetin is fused with potash, salicylic acid is formed. The authors confirm Stenhouse's observations that datiscetin is converted into picric acid on treatment with concentrated nitric acid, and into nitrosalicylic acid (m. p. 226°), on treatment with dilute nitric acid. They conclude that the nitrosalicylic acid has the constitution $[COOH : OH : NO_2 = 1 : 2 : 5]$. It appears probable that when datiscetin is distilled with zinc dust methylphenylenic oxide is formed, whilst if boiled with hydriodic acid (sp. gr. 1.7), methylic iodide is produced, together with a compound melting at 130°, and having the composition of a tetrahydroxanthone, $C_6H_4 \langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \rangle C_6(OH)_4$. Taking the whole of the above-described facts into account, the authors submit the formula $C_6H_4 \langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \rangle C_6(OMe)_3(OH)_3$, $[(OMe)_3 : (OH)_3 = 1 : 2 : 3 : 4]$ as representing the probable constitution of datiscetin. A. R. L.

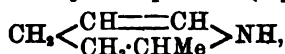
Santonin. By A. ANDREOCCHI (*Ber.*, 26, 2985—2986).—The formula for santonin, which, according to Klein (*Ber.*, 26, 2506), the author has quoted (*Abstr.*, 1893, i, 526) incorrectly from the paper by Cannizzaro and Gucci, on "Some derivatives of Photosantoninic acid" (*Real. Accad. Linc.*, 1892, ii, 149), accurately expresses all that has been proved concerning the constitution of santonin, and only differs from that put forward by Cannizzaro in the nature of the lactone combination, which is acknowledged by the last named chemist to be still an open question. A. H.

Santonone. By G. GRASSI-CRISTALDI (*Ber.*, 26, 2988—2990).—The author points out that Klein (this vol., i, 51) is in error in employing the formula $(C_{15}H_{13}O_2)_2$ for santonone instead of $(C_{15}H_{17}O_2)_2$, and further maintains the accuracy of his original observation that the melting point of santonone is 223°, and not 200—201° as stated by Klein. The resulting questions raised by Klein will be found answered in the author's original communication on the subject (*Abstr.*, 1893, i, 110). A. H.

Oxidation of Piperidine and of α -Pipicoline by Hydrogen Peroxide. By R. WOLFFENSTEIN (*Ber.*, 26, 2991—2998; compare *Abstr.*, 1892, 1484).—Amidovaleraldehyde, prepared in the manner previously described, on extraction with ether from acid solution, forms crystals which melt at 39° and boil at 110—111° under 55 mm. pressure. The *phenylhydrazone acetate*, $C_{13}H_{21}N_3O_2$, is crystalline and melts at 130°. By the action of hydrogen peroxide in excess on piperidine, formic and butyric acids are formed in addition to glutaric acid. On reducing amidovaleraldehyde with zinc and

hydrochloric acid, piperidine is regenerated. With nitric acid, the aldehyde forms a *nitrate*, but the slightest excess of acid converts the aldehyde into succinic acid. *α-Piperidinesulphonic acid*, $C_6H_{10}SO_3H$, is formed from sodium hydrogen sulphite and amidovaleraldehyde hydrochloride, and crystallises in prismatic needles melting at 180° . The compound has no reducing properties and does not react with iodine and starch; on heating with fuming nitric acid and barium chloride, barium sulphate is precipitated. The *sodium salt* is readily soluble, and is formed from sodium hydrogen sulphite and amidovaleraldehyde.

Amidocaproaldehyde, $NH_2 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHO$, is prepared by the action of hydrogen peroxide on *α*-pipecoline at ordinary temperatures for 48 hours. It boils at $116-117^\circ$ under 60 mm. pressure, and closely resembles amidovaleraldehyde in properties and reducing powers. The *hydrochloride*, $C_6H_{13}NO \cdot HCl$, which can be crystallised from a mixture of acetone and alcohol, melts at 116° . By the prolonged action of hydrochloric acid on amidocaproaldehyde, it is converted into secondary tetrahydro-*α*-picoline (*α*-pipecoleine),



which is also formed by distillation of the aldehyde with potash; it boils at $123.5-125.5^\circ$ under a pressure of 750 mm. and is probably identical with the compound obtained by Ladenburg by the action of bromine on *α*-pipecoline. The hydrochloride crystallises in colourless needles melting at 204° . The picrate is oily.

In addition to amidocaproaldehyde, the oxidation of *α*-pipecoline gives rise to a ketonic or aldehyde acid in small quantity; it is contained in the residue after the steam distillation of the aldehyde. It crystallises from a mixture of alcohol and acetone in stellate groups of colourless needles, melts at 103.5° , and has one or other of the formulæ $CHO \cdot CH(NH_2) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$;



With hydrogen peroxide in excess, *α*-pipecoline yields formic, acetic, and succinic acids. Coniine and *β*-pipecoline closely resemble *α*-pipecoline in their behaviour towards hydrogen peroxide, *α*-picoline is much more stable, and even after a considerable time only yields small quantities of formic acid. These results, as well as the numerous syntheses of pyridine derivatives which are known show how close the connection is between this class of compounds and the members of the fatty series, and render it easier to understand the formation of pyridine compounds (alkaloids) by plants. J. B. T.

Synthesis of Hydroquinoline Derivatives. By I. GUARESCHI (*Chem. Centr.*, 1893, ii, 454; from *Atti Accad. Sci. Torino*, 1893).—Ethylic cyanacetate readily acts on orthamidoacetophenone forming a substance which crystallises in silky needles, melts at $330-332^\circ$, and has the composition $C_{11}H_8N_2O$. It is *β*-cyano-*α*-methylpseudo-carbostyryl, or *β*-cyanolepidone, $C_6H_4 < \begin{array}{c} CMc \cdot C \cdot CN \\ NH \cdot CO \end{array}$; in its formation

the two compounds unite with elimination of alcohol, the cyan-orthamidoacetophenone thus obtained undergoing intra-molecular condensation with loss of water. β -Cyanolepidone is almost insoluble in water, sparingly soluble in alcohol, and with silver salts yields the *silver* compound $C_{11}N_2H_7OAg$. On distillation with zinc dust, it is converted into lepidine, thus confirming the formula already given.

If orthamidobenzaldehyde is substituted for the acetophenone derivative, the corresponding *cyanopseudocarbostyryl*, or β -cyano-*ketodihydroquinoline*, $C_8H_4 < \begin{smallmatrix} CH \cdot C \cdot CN \\ NH \cdot CO \end{smallmatrix}$, is obtained; this crystallises in long needles or lustrous, yellowish plates, melts at $329-331^\circ$ with decomposition, and yields a *silver* compound $C_{10}H_5N_2OAg$.

H. G. C.

Pyrazolidone. By R. v. ROTHENBURG (*Ber.*, 26, 2972-2975).—Hydrazine hydrate acts on acrylic acid with formation of pyrazolidone, $CO < \begin{smallmatrix} NH \cdot NH \\ CH_2 \cdot CH_2 \end{smallmatrix}$; this boils at $132-135^\circ$, has a sharp, pyrazolone-like smell, and is insoluble in alkalis, but soluble in acids. Ferric chloride converts it by oxidation into pyrazolone, and nitrous acid into isonitrosopyrazolone (*Abstr.*, 1893, i, 611). It instantly reduces ammoniacal silver solution.

Phenylhydrazine reacts in a similar manner with acrylic acid, 1-phenylpyrazolidone, $CO < \begin{smallmatrix} NPh \cdot NH \\ CH_2 \cdot CH_2 \end{smallmatrix}$, being produced. This substance separates from benzene in crystals melting at $119-121^\circ$, and boils at $299-301^\circ$. It has been previously prepared by the action of phenylhydrazine on the β -halogen-propionic acids (C. F. Böhringer Söhne, German Patent, 53834). It behaves towards reagents in the same manner as pyrazolidone, being converted by oxidation into 1-phenylpyrazolone (*Ber.*, 24, 433c), and by nitrous acid into *isonitroso-1-phenylpyrazolone*, $CO \leq \begin{smallmatrix} NPh - N \\ C(NOH) \cdot CH \end{smallmatrix}$, the silver salt of which is a reddish-yellow, granular powder.

A. H.

Action of Halogens on 1-Phenylpyrazole. By O. SEVERINI (*Real. Accad. Linc.*, 1892, ii, 391-394; compare *Abstr.*, 1893, i, 671).—Chlorine acts on 1-phenylpyrazole suspended in water, either with or without the addition of potash, yielding 1-phenylchloropyrazole, melting at $74.5-75.5^\circ$, which the author has previously prepared by the action of sodium hypochlorite on phenylpyrazole.

The 1-phenyldibromopyrazole, melting at 84° , is obtained on adding bromine to 1-phenylpyrazole suspended in dilute potash (1 per cent.). Iodine has no action on 1-phenylpyrazole at 100° under ordinary conditions; a solution of iodine in potassium iodide acts on the pyrazole in potash solution, with formation of 1-phenyliodopyrazole, $C_8H_7IN_2$. This substance is volatile in a current of steam, and crystallises in small, white needles melting at 76.5° ; it is soluble in alcohol and in ether.

W. J. P.

Synthesis of Compounds containing Carbon-Nitrogen Rings from Orthamidobenzylamine and its Derivatives. By M. BUSCH (*Chem. Centr.*, 1893, ii, 578—584; from *Hab. Schrift. Erlangen*).—The substituted amidobenzylamines are prepared by the reduction of the corresponding nitro-compounds with zinc dust and acetic acid at a low temperature. The derivatives containing an aliphatic alkyl group are liquid and strongly basic in character, whilst the derivatives of the aromatic series are crystalline and less basic, but give stable salts with acids.

Orthamidobenzylamine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2$, is a liquid. *Orthamidobenzylmethylamine*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NHMe}$, is an almost colourless oil, which has a bitter taste and alkaline reaction, and is readily soluble in water. *Orthamidobenzylethylamine* is a yellowish oil. *Orthamidodibenzylamine* is an almost colourless oil, slightly soluble in water, readily in alcohol, &c. *Orthamidobenzylparamisidine*,



crystallises in yellowish-white, lustrous scales melting at 82° . *Orthamidobenzylparaphenylidine*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, crystallises in white, nacreous plates melting at 78° . *Orthamidobenzylparachloraniline*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, crystallises in white, lustrous needles melting at $89\text{--}90^\circ$. *Orthamidobenzylparabromaniline* forms white needles melting at 104° . *Orthamidobenzyl-x-naphthylamine* crystallises in almost white, lustrous plates, with a faint tinge of red, and melts at 134° ; its solutions show a bluish-red fluorescence. *Orthamidobenzyl-β-naphthylamine* forms white, lustrous plates melting at 99° ; its solutions have a bluish-violet fluorescence. Many of the salts of the above compounds are also described by the author, together with the corresponding nitro-compounds and other derivatives.

Orthamidobenzylamine itself condenses with aldehydes to form the corresponding tetrahydroquinazolines, $\text{C}_6\text{H}_4\cdot\begin{matrix} \text{NH}\cdot\text{CHX} \\ \text{CH}_2\cdot\text{NH} \end{matrix}$. The substitution products of the base, on the other hand, form benzylidene compounds of the type $\text{RHN}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CHX}$. The latter are decomposed by dilute mineral acids into their components. When treated with metallic sodium in alcoholic solution, the benzylidene compounds take up 2 atoms of hydrogen, and are converted into the substitution derivatives of the corresponding base,



With the exception of orthamidobenzylparachloraniline and the corresponding bromine derivative, these substances yield di-acid derivatives of the carboxylic acids.

The condensation products of the bases described above with benzaldehyde, salicylaldehyde, formaldehyde, and paranitrobenzaldehyde and their derivatives are also described in the paper.

The nitrobenzylamines, when heated on the water bath with benzenesulphonic chloride, are converted into nitrobenzylaminephenylsulphones of the type $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N}(\text{SO}_2\text{Ph})\text{R}$, and these, on reduc-

tion, yield the corresponding amido-bases, but are not converted into anhydro-compounds.

The orthamidobenzylamines react with carbonyl chloride and with carbon bisulphide to form keto- and thio-derivatives of tetrahydroquinazoline, $C_6H_4 \begin{smallmatrix} NH \cdot CO \\ \diagup \quad \diagdown \\ CH_2 \cdot NR \end{smallmatrix}$ and $C_6H_4 \begin{smallmatrix} NH \cdot CS \\ \diagup \quad \diagdown \\ CH_2 \cdot NR \end{smallmatrix}$. The compounds thus obtained are not identical with those prepared by Söderbaum and Widmann from the corresponding carbamide and thiocarbamide derivatives of orthamidobenzyl alcohol, although, from the method of formation, substances of identical constitution would be expected. The thiotetrahydroquinazolines are converted by the action of freshly precipitated mercuric oxide at 150° into the keto-derivatives. When treated with energetic reducing agents, the thio-derivatives are converted into tetrahydroquinazolines. Both the keto- and thio-compounds are oxidised by permanganate to the same diketo-derivative, $C_6H_4 \begin{smallmatrix} NH \cdot CO \\ \diagup \quad \diagdown \\ CO \cdot NR \end{smallmatrix}$. With the exception of the derivatives prepared from orthamidobenzylamine itself, these keto- and thio-compounds are completely indifferent to acids and bases. Methyl iodide forms the hydriodide of the corresponding methyl derivative, and the compound thus produced has strongly marked basic characters.

Ketotetrahydroquinazoline, $C_8N_2H_8O$, forms either a white, amorphous mass, or indistinct, white, microscopic needles melting at 180° . It is soluble in alcohol and acetic acid, but almost insoluble in water. *Phenylketotetrahydroquinazoline*, $C_8N_2H_7PhO$, crystallises from ethylic acetate in transparent, four-sided plates with an adamantine lustre, and from alcohol, on dilution with water in broad, pointed needles or thick plates. It softens at 186° , and melts at 189° . *Paratolylketotetrahydroquinazoline* crystallises from alcohol in lustrous needles and from ethylic acetate in transparent prisms melting at 218 – 220° ; it is readily soluble in boiling alcohol, but insoluble in water. *Phenethylketotetrahydroquinazoline* forms fascicular groups of colourless needles melting at 223° . *Parabromophenyltetrahydroquinazoline* crystallises in transparent, quadratic plates melting at 226° .

Thiotetrahydroquinazoline, $C_8N_2H_8S$, is prepared by heating orthamidobenzylamine with an excess of carbon bisulphide and an equal volume of dilute alcoholic potash; it forms white, lustrous plates melting at 210 – 212° . *Ethylthiotetrahydroquinazoline* crystallises in white, lustrous plates, melts at 185° , and is very soluble in benzene and chloroform. *Phenylthiotetrahydroquinazoline* forms colourless needles, or large transparent plates, slightly soluble in alcohol, more readily in boiling acetic acid. It softens and becomes yellow at 235° , and melts at about 245° . *Paratolylthiotetrahydroquinazoline* crystallises in white, flat needles, softens at 230° , and melts at 235° . *Phenethylthiotetrahydroquinazoline* separates in white, silky needles melting at 238° . *Parachlorophenylthiotetrahydroquinazoline* forms lustrous, silver-white plates, melts at 228° , and is soluble in carbon bisulphide and boiling acetic acid. *Parabromothiotetrahydroquinazoline* crystallises from absolute alcohol in transparent, four-sided prisms melting at 234° . *a-Naphthylthiotetrahydroquinazoline* crystallises from amyl

alcohol in transparent, lustrous plates melting at 255°. *β-Naphthyl-thiotetrahydroquinazoline* forms brilliant, transparent plates, melts at 280°, and is soluble in acetic acid.

Tetrahydroquinazoline, $C_6H_4 < \begin{smallmatrix} NH \cdot CH_2 \\ CH_2 \cdot NH \end{smallmatrix}$, crystallises in white plates, which are soluble in water, and melts at 81°. *α-Naphthyltetrahydroquinazoline* forms white, lustrous plates, readily soluble in absolute alcohol, &c., and melts at 134°. *β-Naphthyltetrahydroquinazoline* forms yellowish plates melting at 135–139°.

When the substituted orthamidobenzylamines are treated with nitrous acid, the diazo-compounds which are first produced are immediately converted, with elimination of the elements of hydrogen chloride, into phenodihydrotriazines of the type $C_6H_4 < \begin{smallmatrix} N=N \\ CH_2 \cdot NR \end{smallmatrix}$.

Thus *β-phenophenyldihydrotriazine* may be prepared by the action of nitrous acid on orthamidobenzylaniline, and it is also obtained when orthamidobenzylphenylhydrazine is treated with nitrous acid, the nitrosamine of orthamidobenzylaniline, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot NO$, being probably formed as an intermediate product.

β-Phenophenyldihydrotriazine forms lustrous, yellowish plates, and melts at 128° with evolution of gas. *β-Phenomethyldihydrotriazine* separates from boiling light petroleum in yellowish plates, and from ethylic acetate in large, lustrous crystals melting at 72–73°. *β-Phenethyldihydrotriazine* is a yellow oil, and forms salts which crystallise well. *β-Phenobenzoyldihydrotriazine* is precipitated in snow-white needles, on adding water to its alcoholic solution and crystallises in large, six-sided tablets, melting at 91° with evolution of gas. *β-Phenoparatyldihydrotriazine* crystallises from alcohol in yellow, lustrous, rhomboidal plates, and from ether in thick crystals with an adamantine lustre, and melts at 151°. *β-Phenoparanisoyldihydrotriazine* forms lustrous, crystalline scales, and melts with decomposition at 139°. *β-Phenoparaphenyldihydrotriazine* crystallises in golden-yellow, lustrous plates, melting at 144° with evolution of gas. *β-Phenoparachlorophenyldihydrotriazine* separates from hot alcohol in golden plates, and from benzene in thick, transparent crystals melting at 134°. *β-Phenoparabromophenyldihydrotriazine* forms pale yellow, lustrous plates, melting at 164°. *β-Phenacetyldihydrotriazine* separates from alcohol at 60° in lustrous plates, and from ether in flesh-coloured, rhomboidal plates; it softens at 136°, and melts at 138° with evolution of gas. *β-Phenobenzoyldihydrotriazine* forms white, lustrous needles melting at 114–115° with evolution of nitrogen.

The *β-phenodihydrotriazines* are basic compounds, and, with the exception of those containing acid radicles, which are only slightly basic, give stable salts. They are themselves very unstable, melt with evolution of nitrogen, and show a remarkable similarity to the diazo-compounds. In aqueous solution, the salts decompose on heating with evolution of nitrogen and formation of the corresponding hydroxybenzylamine, whilst heating with a concentrated halogen acid leads to the formation of the corresponding halogen derivative. With amines and phenols, they yield the deeply-coloured azo-compounds

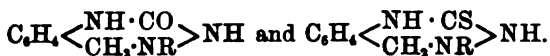
which are characteristic of the diazo-compounds. Thus with β -naphthol, the product is of the type $\text{OH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NHR}$. These colouring matters are acted on by reducing agents in the usual manner. Gentle oxidising agents have, as a rule, no action on the triazines, whilst stronger reagents cause a breaking up of the molecule. On reduction, the phenodihydrotriazines are converted into the corresponding amidobenzylamine, ammonia being eliminated. When β -phenotolyldihydrotriazine is heated at its melting point, nitrogen is evolved, and benzylidenetoluidine, $\text{CHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_7$, is left as an oil.

When the orthonitrobenzyl nitrosamines are reduced, the corresponding amidobenzylhydrazines are formed.

Orthonitrobenzylphenyl nitrosamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$, separates from alcohol in coarse, yellow crystals, and from ether in clear, vitreous prisms melting at 84° . *Orthamidobenzylphenylhydrazine*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NH}_2$, crystallises in vitreous needles melting at 102° . *Orthonitrobenzylparatolyl nitrosamine* forms lustrous, yellow needles melting at 80° . *Orthamidobenzylparatolylhydrazine* crystallises in snow-white, lustrous needles melting at 66° . *Orthonitrobenzylparaphenetylnitrosamine* forms orange-coloured plates melting at 95° . *Orthamidobenzylparaphenetylhydrazine* crystallises in colourless needles or rhomboidal tablets melting at 98° . *Orthonitrobenzylparachlorophenyl nitrosamine* crystallises in yellow, transparent prisms melting at 100° . *Orthamidobenzylparachlorophenylhydrazine* forms transparent prisms melting at 95° . *Orthonitrobenzylparabromophenyl nitrosamine* crystallises in microscopic plates melting at 107° . *Orthamidobenzylparabromophenylhydrazine* forms lustrous tablets melting at 119 – 120° . *Orthonitrobenzyl- β -naphthyl nitrosamine* crystallises in dark yellow plates melting at 102° . *Orthamidobenzyl- β -naphthylhydrazine* forms small needles melting at 76° .

The amidobenzylhydrazines are powerful bases. They reduce Fehling's solution and silver oxide at the ordinary temperature, form very hygroscopic salts with the mineral acids, and condense with aldehydes to form dibenzylidene compounds.

The amidobenzylhydrazines react with carbonyl chloride and carbon bisulphide in a manner similar to the amidobenzylamines, yielding products of the type



These substances melt between 250° and 300° with evolution of gas and decomposition, and are much less stable than the corresponding quinazoline derivatives, into which they tend to pass. The thiocarbamides derived from the amidobenzylhydrazines, for example, when treated with metallic sodium in alcoholic solution, yield the corresponding tetrahydroquinazolines, ammonia and hydrogen sulphide being evolved. These seven-ring compounds are indifferent towards both acids and alkalis. A. H.

Action of Cyanogen on Hydrazine. By A. ANGELI (*Gazzetta*, 23, ii, 103–104).—On passing a rapid current of cyanogen into an

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aqueous solution of hydrazine, and strongly cooling, a *substance* of the composition $C_2N_6H_4$, separates; it forms large prisms which do not melt at 230° . It readily acts on aldehydes and ketones, and may therefore have the constitution $C(NH \cdot NH_2)_2(NH)$. When treated with nitrous acid, it gives a white, crystalline product; this is probably the *ditetrazole*, $\begin{array}{c} N-N \\ || \\ N-NH \end{array} > C \cdot C < \begin{array}{c} N-N \\ || \\ N-NH \end{array}$.

W. J. P.

Sparteïne. By F. B. AHRENS (*Ber.*, 26, 3035—3042; compare Abstr., 1893, i, 232).—The author has already described the formation of trioxysparteïne by the action of hydrogen peroxide on oxysparteïne. If oxysparteïne hydrochloride is treated with dilute hydrogen peroxide, no trioxysparteïne is obtained, but a quantitative yield of a *new base*, $C_{15}H_{24}N_2O_2$, which crystallises from ether in white needles. The *hydrochloride*, $C_{15}H_{24}N_2O_2 \cdot HCl$, crystallises, with $3\frac{1}{2}H_2O$, in white needles. The *dihydrochloride*, $C_{15}H_{24}N_2O_2 \cdot 2HCl + 3\frac{1}{2}H_2O$, crystallises in transparent prisms. The *hydrobromide*, $C_{15}H_{24}N_2O_2 \cdot HBr + 4H_2O$, forms transparent crystals. The *platinochloride*,



crystallises in orange leaflets or needles, and decomposes at 236° . The *aurochloride* crystallises in lustrous leaflets, darkens at 186° , and melts at 194° with decomposition.

A *base* of the composition $C_{15}H_{24}N_2O$ is obtained by boiling sparteïne with freshly prepared silver oxide or mercuric oxide and water. It is an oil which quickly darkens on exposure to air. The *hydroiodide*, $C_{15}H_{24}N_2O \cdot HI$, crystallises in leaflets, and melts at 211° . The *platinochloride* forms small, sparingly soluble crystals, and melts at 108° . The *aurochloride* forms microscopic crystals, and melts at 175° with decomposition.

A *base* isomeric with the preceding is obtained by boiling sparteïne with freshly prepared lead peroxide and water. It is a hygroscopic resin, easily soluble in water. The *platinochloride* forms small crystals, darkens at 230° , and decomposes at 256° . The *aurochloride* is a crystalline powder, and melts at 178 — 180° with decomposition.

Dehydrosparteïne, $C_{15}H_{24}N_2$, is obtained by shaking sparteïne with a concentrated solution of bleaching powder. It is a liquid closely resembling sparteïne, and boils at 314 — 316° (uncorr.) without decomposition. The *hydrochloride*, $C_{15}H_{24}N_2 \cdot 2HCl + 2\frac{1}{2}H_2O$, forms large, colourless crystals resembling ammonium chloride, and carbonises at 270° . The *hydrobromide* crystallises with $1H_2O$. The *hydroiodide*, with $1H_2O$, melts at 258° . The *platinochloride*, with $2H_2O$, crystallises in beautiful, indented plates, and melts at 237° with decomposition. The *aurochloride* crystallises in sparingly soluble needles, gradually blackens when heated, and froths up at 168° .

Sparteïne sulphate, when distilled under 16—20 mm. pressure with zinc-dust and zinc oxide, yields a mixture of bases, namely, diethylmethylamine, pyridine, α -picoline, a base which was not identified, 2:3:6-trimethylpyridine, sparteïne, and a *base* of the formula $C_{16}H_{26}N_2$, which melts at 99 — 101° , and yields an *aurochloride* melting at 190° with decomposition.

E. C. R.

Meconinemethyl Methyl Ketone and Di-meconinemethyl Ketone. By F. HEMMELMAYR (*Monatsh.*, 14, 390—399).—Meconine-

methyl methyl ketone, $\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_5(\text{OMe})_2 \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{COMe}$ (Abstr., 1892, 179), is hydrolysed by boiling baryta water partly into the hydroxy-acid by severance of the lactone bond, and partly into opianic acid and acetone. When, however, a mixture of opianic acid and acetone is boiled with baryta water, condensation occurs, and meconinemethyl methyl ketone is formed. The ketone is hydrolysed by alkaline permanganate also into opianic acid and acetone, the latter substance being of course further oxidised to formic acid. The hydrolysis is not due to the action of the alkali. The *phenylhydrazone* is described; it melts at 159—160°. Meconinemethyl methyl ketone is converted by boiling bromine water into a *monobromo-derivative*.

Di-meconinemethyl ketone, $\text{CO}[\text{CH}_2 \cdot \text{CH} < \begin{array}{c} \text{C}_6\text{H}_5(\text{OMe})_2 \\ \text{O} \end{array} > \text{CO}]_2$ (*loc. cit.*), is hydrolysed by boiling baryta water in the same way as the mono-compound.

The author claims priority in the preparation of a phenylhydrazine-lactone additive compound, namely, the dihydrazone of meconinemethyl phenyl ketone (Abstr., 1893, i, 181). JN. W.

Action of Methylic Iodide on Papaverinic acid. By F. SCHRANZHOFER (*Monatsh.*, 14, 597).—The author finds that the normal barium salt of the methylbetaine of papaverinic acid, $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_4 \cdot \text{Ba}$ (this vol., i, 59), crystallises with $6\text{H}_2\text{O}$.

G. T. M.

Cinchonine. By M. FREUND and W. ROSENSTEIN (*Annalen*, 277, 277—290).—A preliminary account of the author's experiments has already been published (Abstr., 1892, 892).

The specific rotatory power of dimethylcinchonine dihydrochloride, that is, of the basic hydrochloride (*loc. cit.*), dissolved in dilute hydrochloric acid is $[\alpha]_D = +5.37^\circ$ at 20° . When to the last-mentioned solution platonic chloride is added, a *platinochloride*,



is precipitated. The hydrobromide, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O} \cdot \text{HBr}$, melts at $118\text{--}120^\circ$ (not 111° ; *loc. cit.*). The *picrate*, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O} \cdot 2\text{C}_6\text{H}_5\text{N}_3\text{O}_7$, melts at 160° ; the *zincchloride*, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O} \cdot \text{H}_2\text{ZnCl}_2$, melts at 220° ; and the *mercuriochloride* at 222° . *Dimethylcinchonine ethiodide* melts at 138° ; *dimethylcinchonine benzylic chloride* was prepared.

Methylcinchonine, dimethylcinchonine, methylcinchonine methosulphate, and dimethylcinchonine methosulphate all yield cinchoninic acid when oxidised by Skraup's method (*Annalen*, 201, 291); this fact shows that the alkyl groups are combined with one and the same nucleus.

When dimethylcinchonine methiodide is boiled with concentrated alkali, it decomposes into trimethylamine, and a *base* which yields a yellow, amorphous *platinochloride*, $(\text{C}_{19}\text{H}_{19}\text{NO})_2 \cdot \text{H}_2\text{PtCl}_6$, that does not melt at 280° .

The presence of a quinoline nucleus explains how the nitrogen atom in one-half of the molecule of cinchonine is combined, whereas the function of the second nitrogen atom is still obscure.

A. R. L.

Pseudocinchonine. By E. LIPPMANN and F. FLEISSNER (*Monatsh.*, **14**, 371—375).—When cinchonine trihydriodide is heated with water ($\frac{1}{2}$ to $\frac{3}{4}$ vol.) for 5—6 hours at 150—160°, it gradually dissolves, and, on keeping the solution, a yellow, acicular precipitate gradually falls, consisting of the hydriodide of pseudocinchonine, a base isomeric with cinchonine.

The base may be isolated by means of the sparingly soluble normal sulphate. The product of the above action is precipitated with ammonia, and the mixed bases suspended in water and cautiously neutralised with dilute sulphuric acid. Pseudocinchonine sulphate soon separates, whilst the sulphates of cinchonine and isocinchonine remain in solution. The free base is precipitated by ammonia from the hot aqueous solution.

Pseudocinchonine, $C_{19}H_{23}N_2O$, is a white, flocculent or granular substance melting at 214—216° (cinchonine melts at 250—252°, and isocinchonine at 126—127°). It is soluble in ether, and may be thus readily separated from cinchonine. The *normal sulphate* forms long, slender, asbestos-like needles, and, unlike the corresponding salts of cinchonine and its other isomerides, is anhydrous. The *platinochloride* and *dihydriodide* are described. J. N. W.

Chitenine. By R. v. BUCHER (*Monatsh.*, **14**, 598—611).—When chitenine, the oxidation product of quinine, is heated for two hours with $2\frac{1}{2}$ times its weight of benzoic chloride, the *benzoyl derivative*, $C_{18}H_{21}N_2O_4Bz$, is obtained. It is readily soluble in alcohol, ether, and benzene, and is precipitated by light petroleum from its benzene solution in the form of a pale yellow powder, which melts at 85°. The *platinochloride*, $C_{18}H_{21}N_2O_4Bz, H_2PtCl_6$, is a bright yellow, crystalline powder. The *platinochloride*, $C_{18}H_{19}N_2O_4Ac_2, H_2PtCl_6 + 3H_2O$, obtained from the *acetyl derivative* of chitenine is also a microcrystalline powder.

On passing hydrogen chloride through a cooled solution of chitenine in absolute alcohol, the *ethyl derivative*, $C_{18}H_{21}N_2O_4Et$, is obtained; it crystallises in needles, melts at 198°, and unites with ethylic iodide to form the compound $C_{18}H_{21}N_2O_4Et, EtI$, which crystallises from alcohol in slender, white prisms, and melts at 210°.

Chitenol, $C_{18}H_{20}N_2O_4 + H_2O$, is obtained on heating chitenine with 10 times its weight of colourless hydriodic acid for three hours at 100°. It crystallises from hot water, in which it is only sparingly soluble, in slender, white needles; dissolves readily in acids and alkalis, decomposes at 270°, without previously melting, gives the quinine reaction with chlorine water and excess of ammonia, and yields the following salts:—The *sulphate*, $C_{18}H_{20}N_2O_4, H_2SO_4 + H_2O$, is fairly soluble in water, and crystallises in slender, bright yellow scales; the *hydrochloride*, $C_{18}H_{20}N_2O_4, 2HCl + H_2O$, crystallises in plates, and the *platinochloride*, $(C_{18}H_{20}N_2O_4), 2HCl, H_2PtCl_6$, in yellow

prisms. On oxidising chitenol with alkaline permanganate, products are formed from which two calcium salts can be obtained. Of these, one is insoluble, and contains per cent., C, 35.69; H, 2.36; Ca, 16.59. The other is readily soluble and contains per cent., C, 40.04—42.25; H, 2.65—4.10; Ca, 12.36—13.83; N, 5.43. G. T. M.

Alkaloids of Belladonna. By O. HESSE (*Annalen*, 277, 290—300; compare Abstr., 1891, 748; 1892, 1498).—Merck (Abstr., 1892, 1255) stated that atropamine was identical with Pesci's apotropine (Abstr., 1882, 740); he has since shown (Abstr., 1893, i, 491) that the latter alkaloid, like atropamine, may be converted into belladonnine.

Apoatropine could not be prepared by following Pesci's directions, but is obtained without secondary products when a solution of atropine sulphate in nitric acid of sp. gr. 1.381 is kept at the ordinary temperature for 24 hours; or when atropine sulphate or hyoscyamine sulphate is dissolved in concentrated sulphuric acid in the cold, and the solution poured into water; or when the last-named salts are heated at 85° with acetic, benzoic, or phosphoric anhydride; but not when they are treated under any circumstances with hydrochloric acid. The base is difficult to obtain in a crystalline condition, and the author now confirms Merck's observations (*loc. cit.*), that it is identical with atropamine.

Belladonnine is obtained when a solution of atropine or of hyoscyamine in concentrated sulphuric acid is allowed to remain for a short time. The platinochloride melts at 229°, and the aurochloride at 120°. If hyoscyamine is slowly raised to a temperature of 120—130°, it is first converted into atropine, thence into apoatropine, and finally into belladonnine. When apoatropine is treated with alkalis or with hydrochloric acid, it is converted either into belladonnine or decomposition products of the latter, or undergoes more advanced decomposition; the reason therefore that both Pesci and Merck obtained tropine from apoatropine was, that they subjected the alkaloid to too violent treatment with alkalis, and thus precluded the formation of belladonnine.

When apoatropine is heated in a sealed tube with fuming hydrochloric acid (8 parts) for eight hours at 85—100°, belladonnine and tropine are formed; if, however, the solution is heated for 16 hours at 140°, bellatropine is obtained. The platinochloride, $C_8H_{11}NO_2 \cdot H_2PtCl_6$, melts at 212°, and the aurochloride at 163°. The base crystallises in colourless prisms. A. R. L.

Hyoscine. By O. HESSE (*Annalen*, 277, 304—308; compare Abstr., 1893, i, 679).—The author brings forward fresh evidence in support of the following views. Ladenburg's hyoscine is identical with scopolamine; it has the composition represented by the formula $C_{17}H_{21}NO_4$, and on decomposition at 60—100° yields oscine, $C_8H_{11}NO_2$, which is identical with scopoline. Scopolamine (hyoscine) hydrobromide is therefore not a new mydriatic. A. R. L.

Melting Point of Cocaine Hydrochloride. By O. HESSE (*Annalen*, 277, 308—309; compare Abstr., 1893, i, 679).—When cocaine hydrochloride is heated at 160—161° in a Roth's apparatus, it sinters at the end of 15 minutes, swells up after 25 minutes, and is completely fused in 31 minutes; these changes take place, although more slowly, even at as low a temperature as 152—154°.

A. R. L.

Alkaloids from the Rind of Pomegranate Root. By G. CIAMICIAN and P. SILBER (*Ber.*, 26, 2738—2753; compare Abstr., 1893, i, 287).—Pseudopelletierine appears to be a ketoamine; it does not contain hydroxyl or methoxyl, and is probably a higher homologue of tropine, which it closely resembles. Their experimental results are insufficient to enable the authors to suggest a constitutional formula for the base; they propose the term *granatonine* in place of pseudopelletierine, so as to bring the nomenclature of the derivatives into uniformity with those of tropine.

The production of *granatoline*, $C_8H_{17}NO$, from granatonine (pseudopelletierine) has been previously described (*loc. cit.*); the reduction is more readily accomplished by means of sodium and alcohol than by sodium amalgam and water; it forms feathery, colourless crystals, melts at 100°, boils at 251° under 761 mm. pressure, and does not combine with hydroxylamine. The yield is theoretical. The *hydrochloride* is hygroscopic. The *aurochloride* melts at 213° with previous softening, not at 203°. The *methiodide*, $C_8H_{15}NO, MeI$, crystallises in colourless cubes melting at 307°; on distilling it with potash, the base is regenerated. The *benzoyl derivative* was analysed in the form of its *platinochloride*, $(C_8H_{15}NOBz)_2, H_2PtCl_6$, which is yellow and crystalline.

Granatenine, $C_8H_{15}N$, is prepared by the action of hydriodic acid and phosphorus on granatoline; it is a viscid liquid of somewhat unpleasant odour, and boils at 186° under a pressure of 751 mm. The *aurochloride*, $C_8H_{15}N, HAuCl_4$, is obtained in stellate crystals melting at 220° with decomposition. The *methiodide*, $C_8H_{15}N, MeI$, crystallises in cubes which are not melted at 315°. On distillation with potash, the methiodide undergoes a similar decomposition to that of tropidine methiodide with formation of *methylgranatenine*, $C_8H_{14}NMe$; this closely resembles β -methyltropidine, and boils at 210—220°. The *aurochloride*, *picrate*, and *methiodide* are crystalline and unstable.

Granataldehyde, $C_8H_{13}O$, the analogue of tropilen, is formed, together with dimethylamine, by heating the preceding base in hydrochloric acid solution; it is a nobile, readily soluble liquid, with an aromatic odour, boils at 200—201° under 758 mm. pressure, and readily reduces ammoniacal silver solution. The *phenylhydrazone* is an oily, unstable liquid; an additive compound is formed with hydrogen sodium sulphite, but could not be isolated. The *dibromide*, $C_8H_{13}OBr_2$, is formed at 0°, and crystallises from light petroleum in colourless needles melting at 100°.

Granatyl iodide, $C_8H_{15}NI, HI$, is occasionally obtained as a bye-product in the preparation of granatenine (see above), but the exact conditions necessary for its formation remain undetermined. It is

deposited from water in colourless, feathery crystals melting at 200° with decomposition, blackens on exposure to light, and is readily converted into granatenine on treatment with alkalis.

By the action of hydriodic acid and phosphorus on granatenine or granatoline at 240° for 8–12 hours, two bases are formed; the one is termed granatanine, the other, which corresponds to “norhydro-tropidine,” is called norgranatanine. *Granatanine*, $C_8H_{11}N$, is a camphor-like substance with an odour resembling that of coniine; it melts at $49-50^{\circ}$, boils at $192-193^{\circ}$ under 763 mm. pressure, is readily soluble in water, and has a strongly alkaline reaction. The *aurochloride*, $C_8H_{11}N, HAuCl_4$, crystallises in feathery, pale yellow needles melting at 229° . *Norgranatanine*, $C_8H_{11}N$, was obtained in small quantity, and separated from the preceding base by means of its crystalline carbamate. The *aurochloride* is deposited in yellow plates which melt at 225° .
J. B. T.

Ipecacuanha. By B. H. PAUL and A. J. COWNLEY (*Pharm. J. Trans.*, 53, 61–63).—The so-called “emetine” is a mixture of at least two different alkaloids, the greater part being an amorphous substance, of marked alkalinity, and forming definite neutral salts, which are also amorphous, and cannot be obtained crystalline by any means yet tried. The amorphous alkaloid is associated with others that are distinctly crystalline, and much less soluble in ether, chloroform, or benzene. In the stem of Brazilian ipecacuanha, a crystalline alkaloid is present in a larger proportion, relatively to the amorphous alkaloid, than in the root. The authors are seeking means of separating the alkaloids with the view of determining their several amounts and their chemical and therapeutic properties. They find that the quantity of the mixed alkaloids obtainable from different samples of ipecacuanha root does not vary much from 2 per cent.
R. R.

Alkaloids of Pereiro Bark. By O. HESSE (*Annalen*, 277, 300–302).—The author found (*Annalen*, 202, 141) that pereiro bark contained, besides geissospermine and pereirine, another alkaloid which appears to be identical with that described by Freund and Fauvet (*Abstr.*, 1893, i, 446) under the name of geissospermine. It differs from the author's geissospermine in having a higher melting point (189°). Both dissolve in nitric acid with a purple-red colour, but the coloration produced by Freund and Fauvet's base is more persistent. The same remarks apply to the behaviour of the two compounds with an acid solution of molybdic sulphate; the colourless solution of Freund and Fauvet's base becomes intensely purple-red when heated. Geissospermine hydrochloride is amorphous, but the hydrochloride of the other base is crystalline; other differences are recorded.
A. R. L.

Nucleic Acid. By L. LIEBERMANN and B. v. BITTÓ (*Chem. Centr.*, 1893, ii, 649; from *Centr. Med. Wiss.*, 1893, 465–467).—The nucleic acid prepared from beer yeast by Altmann's method may be shown by the test proposed by Liebermann to contain metaphosphoric acid.

The analysis of the baryta precipitate gave, after subtraction of the organic matter, Ba 48.87, PO₄ 51.12 per cent. Although the composition calculated for Ba(PO₃)₂ is Ba 46.44, and PO₃ 53.56 per cent., the authors believe that the relation of Ba to PO₃ can only correspond with barium metaphosphate. Kossel has also come to hold the view which he formerly opposed, that the phosphoric acid in nucleic acid is present in the form of metaphosphoric acid. It is not necessary to submit nucleic acid to a prolonged digestion, or to any severe treatment, in order to obtain xanthine substances. A. H.

Thymin; a Decomposition Product of Nucleic acids. By A. KOSSEL and A. NEUMANN (*Ber.*, 26, 2753—2756).—The nucleic acids, of which at least four appear to exist, are compounds of an acid with various bases, such as adenine, hypoxanthine, guanine, and xanthine. The nucleic acid prepared from the thyroid gland of calves yields adenine on boiling with water, and is therefore termed adenylic acid. In addition to the adenine, two acids are formed: both are soluble in dilute hydrochloric acid; the one combines directly with albumin to form an insoluble compound, and is, perhaps, the nucleic acid corresponding to paranuclein. The second acid is termed *thymic acid*, it does not precipitate albumin, and, on heating with sulphuric acid (30 per cent.), *thymin*, C₁₁H₁₄N₂O₆, is formed. This substance has neither basic nor acidic properties; it decolorises bromine water, sublimes without decomposition, melts above 250°, and is deposited from water in quadratic and hexagonal crystals. Thymin is also obtained in small quantity by heating adenylic acid. The authors differ from L. Liebermann, who regards the nucleins as compounds of albumin with metaphosphoric acid; they consider that this view is disproved by the production of thymin. J. B. T.

Glucoside Constitution of Proteid Matter. By F. W. PAVY (*Proc. Roy. Soc.*, 54, 54—57).—By the action of potash on proteid matter (purified coagulated egg albumin), the author has obtained a product which forms a hard, glassy mass when dry, gives readily a clear solution with water, yields no coloration with iodine, and does not reduce Fehling's solution. It is precipitated by absolute alcohol, and closely resembles Landwehr's "animal gum." By the action of mineral acids, it is converted into a substance which reduces Fehling's solution; this substance presents the appearance of a sugary extractive, and has a pronounced baked sugar odour. It is very soluble in water, but only slightly so in absolute alcohol; it is readily diffusible, and dissolves cupric hydroxide in presence of excess of potash without producing a biuret reaction. Heated on the water bath for 2 to 3 hours with phenylhydrazine and acetic acid, it gives a crystalline osazone, and has the characteristics of a sugar. It seems to be optically inactive, or possibly very slightly levorotatory.

J. W.

Organic Chemistry.

Cryoscopic Behaviour of Substances of Similar Constitution to the Solvent. By F. GARELLI (*Gazzetta*, 23, ii, 354—382).—Ferratini and Garelli (Abstr., 1893, 156; 512) have already studied numerous cases of abnormal depression of the freezing points of various solvents produced by a number of substances; the cause of this anomalous behaviour was found in the similarity of constitution which exists between the solvent and the substance in such cases, which leads to the formation of solid solutions (compare Van Bijlert, Abstr., 1891, 1411).

Quinoline and isoquinoline give much too high values for the molecular weight in naphthalene solution, although the former base exercises the normal depression on the freezing point of benzene. Acridine gives too high a molecular weight in phenanthrene solution, the depression is normal, however, in benzene and in naphthalene; the author supposes that a solid solution of acridine in phenanthrene is formed. Pyrroline and tetrahydroquinoline give very high values in naphthalene solution; dihydronaphthalene also gives abnormal values, as would be expected from the fact that this substance is isomorphous with naphthalene. Tetrahydrodiphenyl and α -tetrahydronaphthol also behave abnormally if diphenyl and α -naphthol respectively are used as solvents. Tetrahydrocarbazole gives the normal molecular weight in naphthalene, but alters the freezing point of phenanthrene very slightly, this constant being raised if changed at all. Carbazole gives normal values in diphenylamine.

These facts indicate that the formation of solid solutions, and the consequent vitiation of the results of the molecular weight determinations, are conditioned not so much by similarity in the chemical behaviour of the substances concerned as by similarity in constitution. This view is supported by the normal depressions of the freezing points of phenol by pyrroline; these two substances are somewhat similar in respect to chemical behaviour but totally different in molecular configuration. A possible method is thus indicated for determining the constitution of organic substances. Although the constitution of nicotine is not as yet definitely settled, the old view that this base is hexahydrodipyridyl has been disproved by Pinner and by Blau (Abstr., 1893, i, 489; 736). This is confirmed by the observation that nicotine does not form solid solutions with diphenyl whilst γ -dipyridyl does; the constitution of nicotine should, consequently, not be of the same type as that of dipyridyl.

The high values obtained for the molecular weight of phenol by the boiling point method in benzene are usually attributed to the formation of solid solutions; it is much more likely, however, that the abnormal rise in the boiling point is due to the general tendency of hydroxy-compounds to condense. Very high molecular weights are obtained for resorcinol in benzene and naphthalene solutions, operating by the cryoscopic and boiling point methods respectively.

Chlorobenzene, bromobenzene, and benzonitrile depress the freezing point of benzene almost normally. β -chloronaphthalene and the α - and β -naphthylamines give high results in freezing naphthalene; α -nitronaphthalene, however, depresses the freezing point normally. Benzidine gives the normal molecular weight in phenol.

The solid solutions obtained in the above experiments being only isomorphous mixtures, the constituents of such mixtures should have approximately the same crystalline form. The close relation existing in this respect between phenanthrene and anthracene and between the two naphthols and naphthalene is at once evident from crystallographic data respecting these substances furnished by Negri.

W. J. P.

Nitromethane and its Homologues. By BERTHELOT and MATIGNON (*Ann. Chim. Phys.*, [6], 30, 565—572).—Nitro derivatives are formed from the hydrocarbons of the paraffin series and nitric acid with the development of heat, which is comparable to that observed in the case of nitrobenzene; the high values of their heats of formation explain the stability and fundamental difference between the reactions of the nitro-compounds as compared with those of the ethereal nitrites.

Nitromethane :—Heat of combustion at constant volume + 170.25 cal., and at constant pressure + 169.8 cal. Specific heat (between 23° and 80°) = 0.471. Heat of volatilisation, 6.98 Cal. Heat of formation (calculated), from elements C diamond + H₂ + N + O₂ = CH₃NO₂ liquid + 28.8 Cal.; or CH₃NO₂ gas + 21.8 Cal. Heat of formation from methane and nitric acid CH₄ gas + HNO₃ liquid = H₂O liquid + CH₃NO₂ liquid + 36.7 Cal.; or CH₃NO₂ gas + 29.17 Cal. It is thus seen that the heat of formation of nitromethane is a little less than that of nitrobenzene. Heat of dissolution - 0.60 Cal. Heat of neutralisation + 7.01 Cal. (potassium hydroxide); and + 8.9 Cal. (barium hydroxide).

Nitroethane :—Heat of combustion at constant volume + 322.45 Cal., and at constant pressure + 322.30 Cal. Specific heat 0.451 (between 23° and 95°). Heat of volatilisation + 6.90 Cal. Heat of formation (calculated) from its elements + 38.8 Cal. for the liquid, + 31.8 Cal. for the gaseous compound; from ethane and nitric acid + 43.0 cal. for the liquid, and + 36.0 Cal. for the gaseous compound. Heat of neutralisation (potassium hydroxide) + 10.1 Cal.

A. R. L.

Hexamethylene Dibromide. By W. H. PERKIN, JUN. (*Ber.*, 27, 216—217).—A preliminary notice, published in consequence of the appearance of a paper by Salonina on the same subject (this vol., i, 119). By acting on trimethylene chlorobromide, C₃H₆ClBr, with an alcoholic solution of sodium ethoxide, *chloropropyl ethylic ether*, C₃H₆Cl.OEt, is obtained as a colourless oil, boiling at 132—134°. Metallic sodium condenses it into *hexamethyleneglycol diethylic ether*, C₆H₁₂(OEt)₂, an oil which was not analysed, but was converted by strong hydrobromic acid at 150° into *hexamethylene dibromide*, C₆H₁₂Br₂, an oil boiling at 135—137° under 20 mm. pressure. This, in xylene solution, is condensed by finely-divided metallic sodium to hexamethylene,

$\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$, boiling at 77—80°, previously obtained by Baeyer (this vol., i, 174). C. F. B.

Action of Nitric acid on Nononaphthene. By M. KONOVALOFF (*J. Russ. Chem. Soc.*, 25, 389—429).—When nononaphthene, C_9H_{16} , is heated with nitric acid, it is partially converted into a mononitro-derivative, the yield of which varies greatly with the concentration of the acid, temperature, &c. The author obtained the most favourable results by heating 4 c.c. of the hydrocarbon with 20 c.c. of nitric acid (sp. gr. 1·075) for five hours at 130°. About half of the hydrocarbon is attacked under these conditions, and of this portion 40—50 per cent. is converted into the crude nitro-derivative. A larger yield may be obtained by using a weaker acid or a lower temperature, but the action then proceeds very slowly; on the other hand, boiling in open vessels with strong acid does not give favourable results.

From the crude nitro-product two fractions were obtained, one boiling under 40 mm. pressure at 126—129° (sp. gr. at 20°/0° = 0·9797), and the other at 130—132° (sp. gr. at 20°/0° = 0·9908). Both have the composition $\text{C}_9\text{H}_{17}\cdot\text{NO}_2$, both attack sodium in benzene, are themselves partially dissolved by concentrated potash, and form a pseudonitrole with nitrous acid. The mononitronononaphthene is therefore not homogeneous, but consists of a mixture of a secondary and a tertiary nitro-product. The crude nitro-product gives 20 per cent. of the secondary derivative soluble in potash, and 62 per cent. of the tertiary derivative insoluble in potash.

On reduction with zinc and acetic acid, the higher boiling fraction yielded, besides an amine, a ketone of the formula $\text{C}_9\text{H}_{16}\text{O}$. The amine, $\text{C}_9\text{H}_{17}\cdot\text{NH}_2$, distils mostly at 173—175°, and consists of two isomeric compounds which may be partially separated by crystallisation of their platinochlorides.

The *secondary nitronononaphthene*, $\text{C}_9\text{H}_{17}\cdot\text{NO}_2$, is an almost colourless oil boiling at 224—226°, and does not solidify in a freezing mixture. Its sp. gr. at 20°/0° is 0·9908, and at 0°/0° 1·0043. Its molecular refraction, calculated by means of Lorenz's formula, is 47·40. When bromine is added in excess to its clear solution in caustic potash, the *monobromo-derivative*, $\text{C}_9\text{H}_{16}\text{Br}\cdot\text{NO}_2$, is formed; this is a heavy, colourless oil, sp. gr. at 0°/0° = 1·3330, and at 20°/0° = 1·3112, molecular refraction 54·51. On reduction, secondary nitronononaphthene gives the *secondary amidonononaphthene*, $\text{C}_9\text{H}_{17}\cdot\text{NH}_2$, boiling at 175·5—177·5°, having the sp. gr. 0·8434 at 0°/0°, 0·8273 at 20°/0°, and the molecular refraction 45·62. The chloride, sulphate, and nitrate do not crystallise, but the picrate and platinochloride are crystalline.

Tertiary nitronononaphthene, $\text{C}_9\text{H}_{17}\cdot\text{NO}_2$, boils with some decomposition at 220—225°, and has the sp. gr. 0·9919 at 0°/0°, its molecular refraction being 47·41. It gives Liebermann's reaction, but neither a nitrole nor pseudonitrole. On reduction, it yields the *tertiary amidonononaphthene*, $\text{C}_9\text{H}_{17}\cdot\text{NH}_2$, boiling at 173—175°, and having a sp. gr. of 0·8485 at 0°/0°, and the molecular refraction 45·32. It is slightly

soluble in water. The chloride may be crystallised from light petroleum.

The neutral product obtained on the reduction of the crude nitro-derivative was proved to be a *ketone* having the composition $C_{10}H_{16}O$, and boiling at $180-182^{\circ}$. It is a colourless, mobile liquid of sp. gr. 0.8903 at $0^{\circ}/0^{\circ}$. Its *oxime* boils with decomposition at $220-225^{\circ}$, and seems to consist of a mixture of different substances, as a small quantity of the ketone re-obtained from it boiled at $168-172^{\circ}$.

J. W.

α -Decanaphthene. By ZUBKOFF (*J. Russ. Chem. Soc.*, 25, 382—385).—The fraction of Caucasian petroleum boiling between 160° and 172° consists chiefly of decanaphthenes. The portion boiling at $160-162^{\circ}$ (α -decanaphthene), when chlorinated, gives rise to the compounds $C_{10}H_{15}Cl$, $C_{10}H_{15}Cl_2$, and $C_{10}H_{17}Cl_3$.

The dichloro-derivative, when heated with quinoline, yields a hydrocarbon, $C_{10}H_{16}$, which boils between 162° and 170° , and shows the reactions of a terpene.

The monochloro-derivative (b. p. $206-209^{\circ}$) can be converted into an acetate which boils at $224-230^{\circ}$, and into an alcohol, $C_{10}H_{19}OH$, which boils at about 215° .

A naphthylene, $C_{10}H_{18}$ (b. p. $159-162^{\circ}$), is formed at the same time as the acetate when the monochloride is heated at 210° with sodium acetate and acetic acid.

J. W.

Suberone. By V. MARKOVNIKOFF (*J. Russ. Chem. Soc.*, 25, 364—378).—Suberone (10 grams) is dissolved in absolute alcohol, and to the boiling solution sodium (20 grams) is gradually added. The alcohol is subsequently distilled off and the residue treated with water, when an oil separates; a further quantity of this can be extracted from the aqueous solution by treatment with ether. This oil is a monhydric alcohol, $C_7H_{13}OH$, which the author calls *suberylic alcohol* or *suberol*. It boils at $184-185^{\circ}$ under 755 mm. pressure, and its sp. gr. at $15^{\circ}/15^{\circ}$ is 0.9595. The chloride obtained from it by the action of phosphorus pentachloride boils at $173-175^{\circ}$, is lighter than water at the ordinary temperature, and has the sp. gr. 1.0133 at $0^{\circ}/0^{\circ}$. The urethane, $NHPh \cdot CO \cdot OC_7H_{13}$, melts at 85° , is insoluble in water, but easily soluble in alcohol and in ether.

To obtain *suberoxime*, suberone (50 grams) and hydroxylamine hydrochloride (35 grams) are dissolved in 80 per cent. alcohol, dry powdered soda (40 grams) is then added, and the mixture boiled for 5—7 hours on the water bath. The oxime is liquid at the ordinary temperature, and boils at 230° (751 mm.); on cooling, it solidifies to a mass of crystals which melt at 23° ; its sp. gr. at $20^{\circ}/20^{\circ}$ is 1.0228. It is insoluble in water, but attracts moisture from the air, and becomes liquid. The hydrochloride can be obtained in the form of small, colourless prisms.

Suberylamine, $C_7H_{13}NH_2$, may be obtained from suberoxime by reduction either with sodium in alcoholic solution or with sodium amalgam in alkaline aqueous solution. It is a colourless liquid with a mixed odour of ammonia and hydrocarbons. It boils at 169° (corr.), and only partially mixes with water. The hydrochloride is

obtained as a hygroscopic, crystalline mass, very soluble in water and alcohol, but only slightly so in ether. J. W.

Trehalose. By E. WINTERSTEIN (*Ber.*, 26, 3094—3098).—The author has again investigated the products of the hydrolysis of trehalose, but has been unable to find any other product than glucose. The hydrolysis was effected by heating it with 5 per cent. sulphuric acid for six hours, and the solution, after the removal of sulphuric acid and concentration, fractionally precipitated by alcohol in four stages. The four fractions show all the properties of glucose, and give no evidence of the presence of other hexoses or pentoses. The rotatory power of the first and fourth fractions is lower than that of glucose, but this appears to be due to the presence of a bye-product. Previous investigators have sometimes obtained products having a higher specific rotatory power than glucose, but this was probably due to the presence of unaltered trehalose.

The molecular weight of trehalose, as determined by both Raoult's and Beckmann's methods, agrees with the formula $C_{12}H_{22}O_{11}$. It does not combine with phenylhydrazine, and, therefore, in the combination of the two glucose molecules both aldehyde groups must have undergone alteration. H. G. C.

Desiccation of Starch. By BLOCH (*Compt. rend.*, 118, 146—149).—Starch does not lose the whole of its water, even after many hours' heating at 115°, and a temperature of 155—160° is required in order to expel the last traces. At this temperature, there is little or no conversion into dextrin if the starch is pure, but, even if such conversion took place, it would not affect the estimation of the water. C. H. B.

Starch. By C. J. LINTNER (*Ber.*, 27, 293—296).—In reply to the criticism of Scheibler and Mittelmeier (this vol., i, 107), the author explains the grounds which led him to an independent examination and discussion of the amyloïn theory proposed by Brown and Morris. A. H.

New Carbohydrate from Boletus Edulis. By E. WINTERSTEIN (*Ber.*, 26, 3098—3099).—The fungus *Boletus edulis* contains, in addition to trehalose, a carbohydrate, which may be isolated by warming with sulphuric acid the residue left after the removal of fats and proteïds. The jelly thus obtained is boiled with water, the solution filtered, the filtrate concentrated, and precipitated with alcohol. The carbohydrate is freed from sulphuric acid by treatment with dilute alcohol, and then forms a pale yellow, amorphous mass, which gradually dissolves in 5 per cent. aqueous potash. It is slowly inverted by boiling dilute sulphuric acid, and is coloured yellow by iodine in presence of zinc chloride or concentrated sulphuric acid. Its optical properties could not be ascertained, as it forms opalescent solutions. The author proposes for it the name *paradextran*.

The analysis agrees fairly well with the formula $C_6H_{10}O_5$, and the only product of hydrolysis whose presence could be ascertained was glucose. H. G. C.

Methylenamidoacetonitrile. By R. JAY and T. CURTIUS (*Ber.*, 27, 59—62).—*Methylenamidoacetonitrile*, $\text{CH}_2\text{N}\cdot\text{CH}_2\cdot\text{CN}$, is obtained by adding formaldehyde to a strong solution of potassium cyanide and ammonium chloride and allowing the mixture to remain. It crystallises in lustrous, colourless prisms, melts at $129\cdot5^\circ$, decomposes when boiled, and is easily soluble in dilute mineral acids, but is quickly decomposed in acid solution into formaldehyde and amidoacetonitrile. When boiled with alcoholic hydrochloric acid in a reflux apparatus, it yields ethylic amidoacetate hydrochloride,



Amidoacetonitrile hydrochloride, $\text{HCl}\cdot\text{NH}_2\cdot\text{CH}_2\cdot\text{CN}$, is obtained by treating the preceding compound with alcoholic hydrochloric acid at the ordinary temperature. It crystallises in lustrous tablets, is very hygroscopic, and, when warmed with dilute acid, is quickly converted into glycocine hydrochloride and ammonium chloride. *Amidoacetonitrile* is obtained by shaking the hydrochloride with silver oxide. It is a pale yellow oil, having a characteristic odour, and decomposes when distilled, even in a vacuum. When dissolved in acetic acid and treated with sodium nitrite, it yields a compound which the authors believe to be *diazoacetonitrile*, $\text{N}_2\cdot\text{CH}\cdot\text{CN}$. This is a golden-yellow oil, has an odour resembling that of cyanogen, partially decomposes when distilled in a vacuum, and, when reduced with sodium hydroxide and ferrous sulphate, yields hydrazine sulphate. E. C. R.

Behaviour of Unsaturated Bases towards Hydrogen Chloride. By W. JACOBI and G. MERLING (*Annalen*, 278, 1—20).—Merling showed (*Abstr.*, 1891, 1506) that certain unsaturated bases were converted by hydrogen chloride into pyrrolidine bases; in the present paper, the authors describe the similar transformation of analogous bases.

Dimethyl- β -pipecolinammonium iodide, $\text{CH}_3\langle\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix}\rangle\text{NMe}_2\text{I}$, crystallises from alcohol in stout, well-formed prisms, melts at $196-197^\circ$, and, when treated with moist silver chloride, yields the *chloride*, which is a deliquescent, crystalline mass. The *platinochloride* melts at $258-259^\circ$, and the *aurochloride* at $235-236^\circ$. When dimethyl- β -pipecolinammonium chloride is distilled, methylic chloride and *methyl- β -pipecoline*, $\text{CH}_3\langle\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix}\rangle\text{NMe}$, pass over; the latter is an oil immiscible with water, having the odour of piperidine, boils at $124-126^\circ$, and has a sp. gr. = $0\cdot818$ at 15° . The *platinochloride* melts at $156-158^\circ$.

Methylbutallylcarbindimethylamine,



is prepared by digesting dimethyl- β -pipecolinammonium iodide with moist silver oxide and distilling the resulting hydroxide; it is a colourless oil, having the odour of piperidine, is not miscible with water, boils at $129-130^\circ$ and has a sp. gr. = $0\cdot767$ at 15° . When

the fused hydrochloride is treated with hydrogen chloride, *hydrochloromethylbutallylcarbindimethylamine hydrochloride*,



is formed; the *platinochloride* melts at 77–78°, and the *aurochloride* at 68–70°. If an aqueous solution of the last-named hydrochloride is treated with sodium hydroxide at 0°, a mixture of the *hydrochloro-base* and methylbutallylcarbindimethylamine is produced; the latter is driven over with steam, and the residual alkaline solution is neutralised with hydrochloric acid and evaporated to dryness. Alcohol extracts from this mass *dimethyl- $\alpha\beta$ -dimethylpyrrolidinammonium chloride*, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CHMe} \end{array} > \text{NMe}_2\text{Cl}$; and this, on dry distillation, yields methylic chloride and *methyl- $\alpha\beta$ -dimethylpyrrolidine*, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CHMe} \end{array} > \text{NMe}$, which is a colourless oil having the odour of piperidine; it boils at 111–113°, and its sp. gr. = 0.790 at 15°. The *platinochloride* melts at 179–180°, and the *aurochloride* at 98–99°.

Methylallylacetone, $\text{C}_3\text{H}_5 \cdot \text{CHMe} \cdot \text{COMe}$, is prepared from ethylic methylallylacetate; it is a colourless liquid, having a pleasant odour, boils at 138–140°, and has a sp. gr. = 0.845 at 15°. The *phenylhydrazone* is a yellow oil, and, when reduced with sodium amalgam in warm glacial acetic acid solution, yields *methylbutallylmethylcarbinamine*, $\text{C}_3\text{H}_5 \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{NH}_2$, which is a colourless oil immiscible with water; it has the odour of piperidine, boils at 133–136°, and its sp. gr. = 0.793 at 15°. The *platinochloride* melts with decomposition at 157–158°. The *hydrochloro-base*,



forms a *platinochloride*, melting at 157–158° with decomposition, and, when heated, it is converted into *$\alpha\beta$ -trimethylpyrrolidine hydrochloride*, $\begin{array}{c} \text{CHMe} \cdot \text{CHMe} \\ | \\ \text{CH}_2 - \text{CHMe} \end{array} > \text{NH}, \text{HCl}$. The base is volatile with steam; it is a colourless oil miscible with water, has the odour of piperidine, boils at 126–128°, and its sp. gr. = 0.816 at 15°. The *platinochloride* melts at 205–206° with decomposition.

Allylbutallylmethylcarbinamine, $\text{CH}(\text{C}_3\text{H}_5) \cdot \text{CHMe} \cdot \text{NH}_2$, is prepared by the reduction of diallylacetonephenylhydrazone; it is a colourless oil not miscible with water, has the odour of piperidine, boils at 174–176°, and its sp. gr. = 0.826 at 15°. The *platinochloride* melts at 159–160° with decomposition. The *hydrochloro base*,



is a colourless oil, having a penetrating, unpleasant odour; it forms a *platinochloride*, melting with decomposition at 158–159°. If an ethereal solution of the hydrochloro base is heated, *$\alpha\alpha$ -dimethyl- β -allylpyrrolidine hydrochloride*, $\begin{array}{c} \text{CH}(\text{C}_3\text{H}_5) \cdot \text{CHMe} \\ | \\ \text{CH}_2 - \text{CHMe} \end{array} > \text{NH}, \text{HCl}$, is obtained. The base boils at 174–176°, and its sp. gr. = 0.685 at 15°; the *platinochloride* forms orange-yellow plates. A. R. L.

Compounds of Hexamethylenamine with Hydrogen Bismuthiodide. By H. LEY (*Annalen*, 278, 57—60).—Kraut has shown (*Annalen*, 210, 310) that compounds are obtained from amines and hydrogen bismuthiodide.

Hexamethylenamine hydriodide is precipitated when absolute alcohol is added to mixed concentrated aqueous solutions of hexamethylenamine and hydriodic acid; it separates from aqueous alcohol in large crystals, and melts at 170—171°.

The compound $3(C_6H_{12}N_4, HI), BiI_3$ (A), separates as an orange, amorphous precipitate when a 20 per cent. solution of hexamethylenamine is stirred into a cold 5 per cent. solution of potassium bismuthiodide; the crude precipitate is washed with absolute alcohol, and dried over concentrated sulphuric acid. The same compound is obtained when potassium bismuthiodide is added to an alcoholic solution of hexamethylenamine hydriodide; the presence of water tends towards the production of compounds richer in bismuth. If the precipitate is allowed to remain in contact with an excess of potassium bismuthiodide, it becomes olive-green, but, on being washed with alcohol, again changes to orange; it consists of the compound $2(C_6H_{12}N_4, HI), BiI_3$. When the freshly-precipitated compound (A) is heated with alcoholic hydriodic acid, a portion dissolves, and six-sided plates, having the same composition, are precipitated from the filtrate; the portion remaining undissolved also becomes crystalline, and consists of the compound $2(C_6H_{12}N_4, HI), BiI_3$. If the freshly-precipitated compound (A) is warmed with excess of potassium bismuthiodide, purple microscopic, six-sided plates of the compound $C_6H_{12}N_4, HI, BiI_3$ are obtained.

The stability and characteristic properties of these derivatives render them suitable for the detection of hexamethylenamine.

A. R. L.

Ring Formation in Organic Nitrogen Compounds. By A. MICHAEL (*J. pr. Chem.*, [2], 49, 26—43).—By adding ethylic carbonate to a solution of sodium and guanidine thiocyanate in alcohol and neutralising the liquid after some days, ethylic guanidinedicarboxylate (guanidine diethylcarbonate; Nencki, this Journal, 1875, 754) is precipitated. The filtrate contains guanoline $CN_2H_4 \cdot COOEt$ (*loc. cit.*). When ethylic oxalate is substituted for the carbonate, oxalylguanidine (Traube, this vol., i, 7) is formed, and this is also the product of the action of ethylic oxalate on guanidine itself, but when guanidine carbonate is used, a considerable quantity of *guanidine-ethylic oxalate*, $COOEt \cdot COO \cdot NH_2 \cdot C(NH_2)_2$, may be obtained. This crystallises in cubes, and melts at 134—136° when quickly heated, solidifying again at 165°, when it becomes hydrated oxalylguanidine; it dissolves freely in water, but only sparingly in organic solvents. The reaction between thiocarbamide, sodium ethoxide, and ethylic oxalate produces thioparabanic acid.

Guanidine thiocyanate, sodium ethoxide, and ethylic malonate interact to form malonylguanidine (Traube, *loc. cit.*). When guanidine reacts with ethylic malonate, *guanidine-ethylic malonate* is produced; it crystallises in prisms. With guanidine carbonate, malonylguanidine is formed. The action of ethylic sodiomalonate

on thiocarbamide gives rise to the sodium derivative of thiobarbituric acid.

A compound, $C_7O_2N_2H_{12}$, whose constitution has not been settled, is prepared by mixing sodium ethoxide, guanidine thiocyanate, and ethylic succinate in alcohol; it crystallises in white, prismatic needles, melts with decomposition at $190-191^\circ$, and is freely soluble in hot water. Another compound, $C_{11}H_{22}N_6O_6$, is obtained by the action of guanidine on ethylic succinate; it forms small prisms which do not melt at 300° , and is decomposed by hydrochloric acid with formation of the compound $C_6H_8N_4O_6$, which crystallises in needles, melts at $184-185^\circ$, and dissolves in hot water. When guanidine carbonate is used, *guanidine-ethylic succinate*, $COOEt \cdot CH_2 \cdot CH_2 \cdot COO \cdot NH_2 \cdot CN \cdot H_3$, is formed; this crystallises in prisms, melts at $136-138^\circ$, and is very soluble in water.

The mixture of guanidine thiocyanate and sodium ethoxide, used in the above cases, may be applied to the synthesis of many guanidine derivatives; in this way there have been obtained, with phenylisocyanate, *diphenylcarbaminyguanidine*, $NH_2C(NH \cdot CO \cdot NHPh)_3$, (m. p. $174-175^\circ$); with phthalic anhydride, the derivative,



(m. p. $202-203^\circ$); with benzile, the derivative, $COPh \cdot CPh \cdot N \cdot CN \cdot H_3$, (m. p. above 300°).
A. G. B.

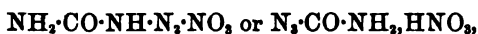
Semicarbazide. By J. THIELE and O. STANGE (*Ber.*, 27, 31-34).—Semicarbazide may be obtained from amidoguanidine or by the action of potassium cyanate on hydrazine sulphate (*Abstr.*, 1892, 1295), and may be isolated in the form of the sparingly soluble compound with benzaldehyde. Benzalsemicarbazide, $NH_2 \cdot CO \cdot NH \cdot N \cdot CHPh$, is best prepared by treating hydrazine sulphate which has been neutralised with sodium carbonate, with a slight excess of potassium cyanate, and leaving it over night. A small amount of hydrazodicarbonamide which separates is filtered off, and the filtrate shaken with benzaldehyde, the precipitate formed being then drained and washed with a little ether. The yield is nearly theoretical. *Acetone-semicarbazide*, $NH_2 \cdot CO \cdot NH \cdot N \cdot CMe_2$, may be obtained in a similar manner by the action of acetone. It is tolerably soluble in cold water, less readily in alcohol, readily in acetone, and crystallises in needles, melting with decomposition at $186-187^\circ$. It is very easily decomposed by mineral acids.

Semicarbazide hydrochloride, $NH_2 \cdot CO \cdot NH \cdot NH_2 \cdot HCl$, is obtained by heating the benzaldehyde compound with fuming hydrochloric acid on the water bath, enough water being added to dissolve the whole mass. The benzaldehyde formed cannot be removed by distillation with steam, as the semicarbazide is thereby decomposed into carbonic anhydride, ammonia, and hydrazine; it must be extracted by shaking with benzene. The hydrochloride separates from a hot aqueous solution on cooling in small needles, and crystallises from alcohol in prisms, melting with decomposition at 173° . It is very soluble in water, less readily in strong hydrochloric acid, and insoluble in alcohol and ether. It is decomposed by continued boiling with acids or alkalis, and its alkaline solution has powerful reducing properties. Cupric chloride

produces a precipitate of a double salt, and platinum chloride is reduced even in acid solution. When the aqueous solution is boiled, a small amount of decomposition into hydrazodicarbonamide and hydrazine occurs. *Semicarbazide nitrate* is obtained by decomposing the acetone compound with nitric acid of sp. gr. 1.4. It is very soluble in water, from which it crystallises in prisms containing water, whilst it separates from alcohol in anhydrous crystals melting at 123° with decomposition. The *sulphate* may be prepared in a similar manner. On precipitating the hydrochloride with sodium picrate, *semicarbazide picrate* is obtained as a yellow mass, which is moderately soluble in water, and crystallises in needles. It melts at about 166°, after some previous decomposition. A. H.

Hydrazides of Carbonic acid and of Thiocarbonic acid. By T. CURTIUS and K. HEIDENREICH (*Ber.*, 27, 55—58).—*Carbamic hydrazide*: *Semicarbazide*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, is obtained by heating a mixture of carbamide and hydrazine hydrate in molecular proportion for three hours in a sealed tube at 100°. It crystallises in colourless prisms, melts at 96°, and reduces Fehling's solution and ammoniacal silver solutions in the cold. When shaken with benzaldehyde it yields benzalsemicarbazide melting at 214°.

Semicarbazide nitrate, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HNO}_3$, is obtained by evaporating semicarbazide with dilute nitric acid at 40°. It crystallises in lustrous tablets, and melts at 125° with evolution of gas. When diazotised, it yields *diazosemicarbazide nitrate*,



which crystallises in lustrous, colourless tablets, melts at 75—76°, yields nitrogen when boiled with dilute sulphuric acid, and does not yield azo-dyes. It probably has a constitution analogous to that of diazoguanidine nitrate as expressed by the second of the above formulæ.

Hydrazinedicarbonamide, $\text{N}_2\text{H}_2(\text{CO}\cdot\text{NH}_2)_2$, is obtained by heating the preceding compound (*Abstr.*, 1893, i, 299). It is more easily obtained by heating carbamide (2 mols.) with hydrazine hydrate (1 mol.) at 130—150°. When oxidised with chromic acid, it yields azodicarbonamide, $\text{N}_2(\text{CO}\cdot\text{NH}_2)_2$.

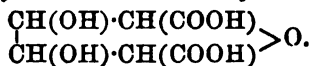
Carbazide, $\text{CO}(\text{NH}\cdot\text{NH}_2)_2$, is obtained by heating ethereal salts of carbonic acid with hydrazine hydrate at 100°. It forms colourless crystals, melts at 152—153°, and combines with 2 mols. of benzaldehyde to form the compound $\text{CO}(\text{NH}\cdot\text{N}\cdot\text{CHPh})_2$, which melts at 198°.

Diammonium dithiocarbazate, $\text{NH}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{SN}_2\text{H}_5$, is obtained by the action of hydrazine hydrate on carbon bisulphide in the cold. It crystallises in white prisms, melts at 124° with decomposition, and decomposes with evolution of hydrogen sulphide in cold aqueous solution, more quickly when warmed. It gives insoluble precipitates with salts of the heavy metals. The *silver salt*, $\text{NH}_2\cdot\text{NH}\cdot\text{CSSAg}$, is a bright yellow powder. The *lead salt* is a lemon-yellow powder.

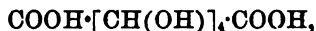
E. C. R.

Isosaccharic acid. By F. TIEMANN (*Ber.*, 27, 118—138).—This acid, obtained from glucosamine or from the chitin of lobster shells,

by oxidation with nitric acid, has been reinvestigated, and found to be, not a tetrahydroxyadipic acid, but the anhydride of such an acid. It is not, however, a lactone, for it is still a bibasic acid; probably it is a dihydroxytetrahydrofurfurandicarboxylic acid,



It, and several of its derivatives, readily unite with 1 mol. of water, yielding an acid, to which the name of *norisosaccharic acid* is given, or derivatives of this acid. These compounds, on their part, readily lose water and regenerate the original substances, and, on this ground, norisosaccharic acid might be regarded as merely a molecular compound of isosaccharic acid with water; the author, however, prefers to regard it, at least provisionally, as a tetrahydroxyadipic acid,



although it is not identical with either of the seven acids of this constitution already known. In preparing metallic salts, norisosaccharates are almost invariably obtained, but these at 100° readily lose their water of crystallisation, if they have any, and also another molecule of water, yielding isosaccharates. A solitary exception is furnished by lead isosaccharate, which can be obtained in anhydrous crystals by adding lead acetate to a hot solution of isosaccharic acid, and allowing the solution to cool. The molecular weight of several derivatives of isosaccharic acid was determined cryoscopically or ebullioscopically, and was found to agree with the above-mentioned view of the constitution of the acid. Further, isosaccharic acid and its calcium salt were found to exhibit birotation.

The following derivatives and salts were prepared. *Diethyllic norisosaccharate*, white needles melting at 73°. *Diethyllic isosaccharate*, melting at 101°. *Dimethyllic norisosaccharate*, melting at 51°. *Diethyllic tetracetyl norisosaccharate*, yellowish-white crystalline mass, melting at 47°, and readily losing acetic anhydride with formation of *diethyllic diacetyl isosaccharate*, which melts at 49°. *Diacetyl norisosaccharic acid*, white needles melting at 174°; at 100° they lose water yielding *diacetyl isosaccharic acid*, which also melts at 174°. The following formulæ represent the metallic norisosaccharates prepared; at 100° they all lose water, and yield the corresponding isosaccharates. $\text{C}_6\text{H}_5\text{O}_5\text{K} + \frac{1}{2}\text{H}_2\text{O}$; $\text{C}_6\text{H}_5\text{O}_5\text{K}_2$. $\text{C}_6\text{H}_5\text{O}_5(\text{NH}_4)$; $\text{C}_6\text{H}_5\text{O}_5(\text{NH}_4)_2$. $\text{C}_6\text{H}_5\text{O}_5\text{Ca} + \text{H}_2\text{O}$. $\text{C}_6\text{H}_5\text{O}_5\text{Sr} + \text{H}_2\text{O}$. $\text{C}_6\text{H}_5\text{O}_5\text{Ba} + \text{H}_2\text{O}$. $\text{C}_6\text{H}_5\text{O}_5\text{Cu} + 3\text{H}_2\text{O}$. $\text{C}_6\text{H}_5\text{O}_5\text{Pb} + \text{H}_2\text{O}$. $\text{C}_6\text{H}_5\text{O}_5\text{Zn} + 3\text{H}_2\text{O}$. $\text{C}_6\text{H}_5\text{O}_5\text{Mg} + 2\text{H}_2\text{O}$. Isosaccharic acid itself forms crystals which melt at 185°; norisosaccharic acid is only known in aqueous solution as a syrup which, when allowed to remain in a vacuum desiccator, slowly deposits crystals of isosaccharic acid. C. F. B.

Glucosamine. By E. FISCHER and F. TIEMANN (*Ber.*, 27, 138—147).—When glucosamine hydrochloride is treated with silver nitrite, a sugar, *chitose*, is formed. This has not yet been isolated, but has been converted by oxidation with bromine into the monobasic *chitonic acid*, which, on oxidation with nitric acid, yields a basic isosaccharic

acid. In a similar manner, bromine oxidises glucosamine hydrobromide to *chitaminic acid*, and the hydrochloride of this, on treatment with silver nitrate, yields *chitaric acid*, which, when oxidised with nitric acid, yielded a quantity of an acid (? isosaccharic) too small to be identified. Heating with hydriodic acid and phosphorus reduces chitaminic acid to an acid, $C_6H_{13}NO_3$ (? amidohydroxycaproic), which melts with decomposition at $220-230^\circ$.

Chitonic acid was obtained as a colourless syrup by concentrating an aqueous solution; it is dextrorotatory, having, in a solution containing also calcium chloride and hydrochloric acid, $[\alpha]_D^{20} = +44.5$. The calcium salt, $(C_6H_{11}O_7)_2Ca$, is also dextrorotatory, having $[\alpha]_D^{20} = +32.8$. The other salts are amorphous.

Chitaminic acid, $C_6H_{13}NO_3$, forms colourless crystals, chars above 250° , and is feebly dextrorotatory. The copper salt, $(C_6H_{13}NO_3)_2Cu$, and the hydrobromide, $C_6H_{13}NO_3.HBr$, were analysed.

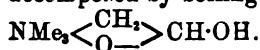
Chitaric acid appears to crystallise, but was not obtained in amount sufficient for purification; it is dextrorotatory. The calcium salt, $(C_6H_7O_6)_2Ca + 4H_2O$, forms colourless crystals. C. F. B.

Polymeric Modifications of Aldehyde. By W. R. ORNDORFF and J. WHITE (*Amer. Chem. J.*, 16, 43—69).—The authors have determined the molecular weight of metaldehyde, making use of Raoult's and Hoffmann's methods, and find that it is identical with that of paraldehyde, namely $(C_2H_4O)_8$. They suggest, therefore, that those two compounds must be represented by the same structural formula in a plane, but that the difference between them may be readily understood if they are regarded as stereo-isomerides; paraldehyde, the more stable modification, being the cistrans, whilst metaldehyde is the cis variety.

When metaldehyde is allowed to remain for a considerable time, the clear, tough, fibrous crystals, which are pulverised with difficulty, become brittle and opaque, and are converted into *tetraldehyde*, $(C_2H_4O)_4$, which is much more stable than metaldehyde, and is characterised by its greater solubility in phenol and thymol. Tetraldehyde closely resembles metaldehyde in its behaviour with reagents, and it may be reconverted into it by dissolving in warm chloroform and cooling the saturated solution in a freezing mixture.

G. T. M.

Amidoacetaldehyde III. By E. FISCHER (*Ber.*, 27, 165—172).—The author has already described the preparation of the aldehyde from acetaltrimethylammonium hydroxide (*Abstr.*, 1893, i, 300). Berlinerblau has also obtained the trimethylammonium derivative of the aldehyde by boiling the acetal compound obtained from trimethylamine and chloroacetal with baryta. The author finds that the two compounds are identical. The aldehyde is not identical with muscarine, its physiological action being very different, and approaching that of choline. When oxidised with silver oxide, it is converted into betaine, and the author therefore names it *betainaldehyde*. It is not decomposed by boiling with bases, and probably has the constitution



Benzoylacetalamine, when allowed to remain in contact with well-cooled, fuming sulphuric acid for a time, yields benzamide. A similar decomposition takes place when hippuric acid is heated with sulphuric acid at 100° .

A *polymeride of amidoacetaldehyde*, $C_6H_{10}N_2O_2$, is obtained by evaporating a mixture of acetalamine and hydrobromic acid to a syrup in a vacuum, and allowing the product to remain for some time over sulphuric acid. The *hydrobromide* so obtained crystallises in colourless, lustrous prisms. The *hydrochloride*, obtained by shaking the hydrobromide with silver chloride, separates in beautiful, colourless crystals. The *platinochloride*, $C_6H_{10}N_2O_2 \cdot H_2PtCl_6 + H_2O$, crystallises in beautiful, yellowish-red prisms or tablets, and decomposes at 200° . The *aurochloride* forms long yellow needles. The *free base*, obtained by shaking the hydrobromide with silver oxide, crystallises in beautiful, long, white needles or prisms, melts about 83° , is extremely hygroscopic, has a strongly alkaline reaction, and is not altered by boiling with alkalis and Fehling's solution. When warmed with concentrated sulphuric acid, it yields a solution which quickly reduces Fehling's solution, and shows all the reactions of the amidoaldehyde. The *dibenzoyl compound*, $C_{18}H_{18}N_2O_4$, crystallises in small needles, darkens at 200° , and melts at $230-250^{\circ}$ with decomposition.

E. C. R.

Hydrazidoacetaldehyde. By E. FISCHER and P. HUNSALZ (*Ber.*, 27, 178—185).—*Hydrazidoacetal*, $NH_2 \cdot NH \cdot CH_2 \cdot CH(OEt)_2$, is obtained by heating hydrazine with absolute alcohol and chloroacetal in an autoclave at $115-120^{\circ}$ for six hours. It boils at $90-100^{\circ}$ under 13 mm. pressure, has a characteristic ethereal odour, is strongly alkaline, and reduces Fehling's solution when gently warmed, and ammoniacal silver solution in the cold. The salts with mineral acids are very soluble in water and alcohol. The *picrate* separates in bright yellow crystals, and melts at $137-138^{\circ}$. The *acid oxalate* crystallises in slender, radiating needles, and melts at 136° with decomposition.

Hydrazidoacetal combines with benzaldehyde or nitrobenzaldehyde to yield oily hydrazones. With nitrous acid, it yields a pale yellow oil, and it also combines with methylic iodide, ethylic acetoacetate, and acetylcarboxylic acid. The *dibenzoylderivative*,



melts at 125° , is easily soluble in alkalis, does not reduce Fehling's solution, and reduces ammoniacal silver solution when heated. *Benzenesulphonohydrazidoacetal*, $SO_2Ph \cdot N_2H_2 \cdot CH_2 \cdot CH(OEt)_2$, obtained by shaking hydrazidoacetal with sodium hydroxide and benzenesulphonic chloride, melts at 68° , and slowly reduces Fehling's solution.

Oxalylidihydrazidoacetal, $C_2O_2[N_2H_2 \cdot CH_2 \cdot CH(OEt)_2]_2$, is obtained by adding ethylic oxalate to an aqueous solution of hydrazidoacetal. It melts at 134° , and reduces Fehling's solution when warmed.

Acetylphenylthiosemicarbazide, $NHPh \cdot CS \cdot N_2H_2 \cdot CH_2 \cdot CH(OEt)_2$, is obtained by gradually adding phenylthiocarbimide to hydrazidoacetal. It crystallises in beautiful, large tablets, melts at $97-98^{\circ}$, and slowly reduces Fehling's solution when warmed. When heated with hydro-

chloric acid, it yields the *hydrochloride* of a base of the composition $C_{11}H_{16}N_2SO, HCl$, melting at 175° with decomposition.

Hydrazidoacetaldehyde hydrochloride, $COH \cdot CH_2 \cdot N_2H_3, HCl$, is obtained by gradually adding hydrazidoacetal to well cooled hydrochloric acid; it decomposes at 98° with violent evolution of gas, very easily reduces Fehling's solution, and yields ammonia when boiled with excess of alkali. The free base was not obtained. When the hydrochloride is treated with sodium acetate, an amorphous, yellow powder is obtained, which has the composition 37.24 per cent. C, 6.88 per cent. H, and 45.33 per cent. N. Glyoxalphenylosazone is obtained on warming the hydrochloride with phenylhydrazine.

E. C. R.

Carbamide Derivatives of Diacetonamine. By W. TRAUBE (*Ber.*, 27, 277—280).—When a salt of diacetonamine is treated with potassium cyanate or thiocyanate, combination takes place, and substances are formed which are anhydrides of the corresponding carbamide derivatives. The constitution of these compounds is to be determined by further researches.

Anhydroadiacetoncarbamide, $C_7H_{12}N_2O$, is obtained by the action of potassium cyanate on diacetonamine oxalate. It crystallises from hot water or benzene in lustrous rhombohedra, melting at 194° .

Anhydroadiacetonethiocarbamide, $C_7H_{12}N_2S$, forms colourless needles, which are insoluble in water, readily soluble in alcohol, and melt at 249° , after becoming brown at a lower temperature.

Diacetonephenylthiocarbamide, $C_{13}H_{18}N_2SO$, is obtained by the direct combination of diacetonamine and phenylthiocarbimide. It forms lustrous plates, melts at 144° , and is slightly soluble in cold water, readily in alcohol. When hydrochloric acid is added to its boiling aqueous solution, the anhydro-compound is precipitated; this forms six-sided prisms, and melts at 191 — 192° . Like anhydroadiacetonethiocarbamide, it is insoluble in alkalis.

A. H.

Constitution of Stearolic acid. By J. BARUCH (*Ber.*, 27, 172—176; see also *Abstr.*, 1893, i, 551).—Stearolic acid,



when treated with concentrated sulphuric acid, yields *ketostearic acid*, $C_8H_{17} \cdot CO \cdot CH_2 \cdot [CH_2]_7 \cdot COOH$. The latter gives with hydroxylamine two stereoisomeric ketoximestearic acids,



When these are treated with concentrated sulphuric acid at 100° , the two acids, $C_8H_{17} \cdot NH \cdot CO \cdot [CH_2]_7 \cdot COOH$ and $C_8H_{17} \cdot CO \cdot NH \cdot [CH_2]_7 \cdot COOH$, are obtained, which, when heated with fuming hydrochloric acid at 180 — 200° , yield octylamine, $C_8H_{17} \cdot NH_2$, sebacic acid, $C_8H_{16}(COOH)_2$, pelargonic acid, $C_8H_{17} \cdot COOH$, and α -amidononanic acid, $NH_2 \cdot [CH_2]_7 \cdot COOH$. A detailed account of the isolation of these acids is given in the original paper.

Ketostearic acid crystallises in white, lustrous leaflets, and melts at 76° . The *ethylic* salt forms beautiful, lustrous, white leaflets, and melts at 41° .

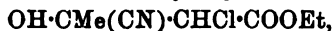
The mixture of *ketoximestearic acids*, obtained by heating the preceding acid with hydroxylamine hydrochloride, sodium hydroxide, and alcohol on the water bath for two hours, forms a white, crystalline mass, stable towards alkalis, and decomposed by boiling with dilute acids into hydroxylamine and ketostearic acid. The mixture of the two acids obtained from them by the action of sulphuric acid melts at 70–80°. E. C. R.

Behenolic acid. By J. BARUCH (*Ber.*, 27, 176–177).—The ethylic salt of the acid obtained by the action of sulphuric acid on behenolic acid has been analysed and gives numbers corresponding with the formula $C_{25}H_{51}\cdot CO\cdot [CH_2]_{12}\cdot COOEt$, thus confirming the author's previous results (*Abstr.*, 1893, i, 551).

Ketobehenic acid, $C_{25}H_{51}\cdot CO\cdot [CH_2]_{12}\cdot COOH$, when treated in the manner described for stearolic acid in the preceding abstract, yields two stereoisomeric ketoximebehenic acids, and finally octylamine, dodecandicarboxylic acid, $COOH\cdot [CH_2]_{12}\cdot COOH$, pelargonic acid, and amidotriskaidecanic acid, $NH_2\cdot [CH_2]_{12}\cdot COOH$. E. C. R.

Halogen Derivatives of Ethylic Acetoacetate. By A. HANTZSCH (*Annalen*, 278, 61–69).—An introduction to Epprecht's paper (next abstract).

Chloro- and Bromo- Derivatives of Ethylic Acetoacetate. By G. EPPRECHT (*Annalen*, 278, 69–87).—The author disproves Haller and Held's observation that ethylic chloracetoacetate yields a mixture of α - and γ -cyanacetoacetates on treatment with potassium cyanide. He confirms Hantzsch and Schiffer's conclusion (*Abstr.*, 1892, 697) that ethylic chloracetoacetate is the α -derivative. The chief product of the action between potassium cyanide and ethylic α -chloracetoacetate in ethereal solution is the *cyanhydrin*,



from which, however, neither citric acid nor ethylic acetonedicarboxylate are formed on hydrolysis. Ethylic α -chloracetoacetate reacts with potassium cyanide in alcoholic solution, forming the potassium derivative of ethylic α -cyanacetoacetate, and a small quantity of a *condensation* derivative, $C_{20}H_{28}N_2O_8$, which is insoluble in alkalis, and melts at 82°.

According to Nef (*Abstr.*, 1892, 143), Duisberg's ethylic bromacetoacetate is a mixture of the α - and γ -derivatives; the author finds, however, in accordance with Hantzsch's observation, that it consists exclusively of the γ -derivative boiling at 125° (10 mm.); it is quantitatively converted into ethylic amidothiazylacetate (m. p. 94°) by means of thiocarbamide.

Schönbrodt's ethylic bromacetoacetate, obtained by brominating the copper derivative of ethylic acetoacetate, is the α -derivative; when treated with thiocarbamide, it is converted into ethylic amidomethylthiazolecarboxylate (m. p. 174°). When ethylic α -bromacetoacetate is treated with potassium cyanide, it yields the α -cyano-derivative (m. p. 26°); whilst ethylic γ -bromacetoacetate under similar treatment forms a compound which is, perhaps, the γ -cyano-

derivative, but which, on distillation in a vacuum, is decomposed into hydrogen cyanide and ethylic succinosuccinate.

Ethylic α -dibromacetoacetate, $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{COOEt}$, is obtained by brominating ethylic γ -bromacetoacetate or its copper derivative; it forms white needles, and melts at $45-49^\circ$.

The copper derivative is a bright, yellowish-green precipitate which melts at 145° .

Ethylic $\alpha\alpha$ -dibromacetoacetate, $\text{COMe}\cdot\text{CBr}_2\cdot\text{COOEt}$, obtained by brominating ethylic α -bromacetoacetate or its copper salt, is an oil; when treated with hydroxylamine, it is converted into Nussberger's ethylic methylsynglyoximecarboxylate (Abstr., 1892, 1175). A. R. L.

Preparation of Suberic Acid. By V. MARKOVNIKOFF (*Ber.*, 26, 3089—3092).—In this paper the author gives the details adopted in the preparation of suberic acid by the oxidation of cork and of castor oil with nitric acid; a yield of 5 per cent. was obtained from the former, and of 13 per cent. from the latter. When impure, suberic acid crystallises from water in indistinct aggregates, but when pure forms microscopic needles, and if allowed to crystallise slowly from a hot incompletely saturated aqueous solution, may be obtained in long, very slender needles, which fall to powder in the air. The pure compound melts at $140-141^\circ$. H. G. C.

Additive Products of Ethylic Sodacetoacetate and Sodiomalonate with Ethereal Salts of Unsaturated Acids. By A. MICHAEL (*J. pr. Chem.* [2], 49, 20—25; compare Abstr., 1892, 590).—The oil resulting from the action of ethylic sodiomalonate on ethylic acetylenedicarboxylate yields aconitic acid when decomposed by baryta water, indicating that the oil has the formula



The action of ethylic acetylenedicarboxylate on ethylic sodethenyltricarboxylate yields a viscid oil,



Ethylic phenylpropiolate and ethylic sodiomalonate yield a pale yellow oil, $\text{COOEt}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CH}(\text{COOEt})_2$, from which a phenylglutaconic acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CH}\cdot\text{COOH}$, crystallising in prismatic plates, and melting at $154-155^\circ$, can be obtained by treatment with baryta water.

Benzalacetone and ethylic sodiomalonate yield the ethylic salt $\text{CH}_2\text{Ac}\cdot\text{CHPh}\cdot\text{CHAc}\cdot\text{COOEt}$, which crystallises in white needles or prisms, melts with decomposition at $155-157^\circ$, and dissolves in organic solvents; when decomposed by potash solution, it yields a colourless oil, $\text{C}_{12}\text{H}_{14}\text{O}$, which boils at $197-198.5^\circ$.

The author concludes with the following generalisation. Unsaturated compounds of the constitution $\text{R}\cdot\dot{\text{C}}\text{H}\cdot\dot{\text{C}}\text{H}\cdot\text{X}$, or $\text{R}\cdot\dot{\text{C}}\cdot\dot{\text{C}}\cdot\text{X}$ [ethylene and acetylene unions being indicated in this way throughout the paper], wherein R is a positive or negative organic radical, and X a strongly negative radical, such as CN, CHO, COOEt, &c., act on ethylic sodiomalonate and sodacetoacetate and their derivatives in

such a manner that the sodium, in accordance with the positive-negative rule, attaches itself to the unsaturated negative carbon, and the remainder of the compound attaches itself to the relatively positive unsaturated carbon atom. A. G. B.

Allofurfuracrylic Acid and the Formation of Allo-Acids. By C. LIEBERMANN (*Ber.*, 27, 283—289; compare *Abstr.*, 1893, i, 513).—Allocinnamic acid, which is formed to the extent of about 5 per cent. when benzalmalonic acid is melted, is not formed at all, or only in traces, when the acid is decomposed at lower temperatures by heating with aniline or quinoline. When benzalmalonic acid is boiled with acetic anhydride, carbonic anhydride is eliminated, and the product contains about 5 per cent. of the allo-acid. The application of this treatment with acetic anhydride to furfuralmalonic acid, on the other hand, resulted in the production of about equal weights of furfuracrylic acid and of its allo-modification. Furfuralmalonic acid, originally prepared by Marckwald (*Abstr.*, 1888, 678), is best obtained by heating furfuraldehyde with malonic acid and glacial acetic acid. It melts at about 205° with decomposition, and not at 187°, as stated by Marckwald. *Furfuracrylic acid* is readily soluble in hot benzene, but dissolves in 77 parts of benzene at 19°. When slowly distilled, it decomposes, with formation of *furfurethylene*, $C_4OH_3CH:CH_2$, which alone passes over into the receiver. This substance is a mobile, colourless liquid, which has an odour resembling that of cinnamene, and boils at 99°. It is insoluble in water, and readily combines with bromine.

Allofurfuracrylic acid is formed, together with the acid just described, when furfuralmalonic acid is heated with acetic anhydride. Like allo-cinnamic acid, it is much more readily soluble than the ordinary form, from which it can therefore be easily separated. It crystallises from light petroleum in needles, and melts indefinitely at 83—87°. The *silver salt* is a white, crystalline precipitate, which is not quite insoluble in water.

The acid readily combines with bromine, and gives a yellowish-red coloration with ferric chloride. Concentrated hydrochloric or sulphuric acid converts it into a resin. When slowly distilled, it yields furfurethylene, but when rapidly heated the distillate contains about 2 parts of furfuracrylic acid to 1 part of the allo-acid. This change proceeds more readily in benzene solution at 170°.

The allo-form of cinnamylacrylic acid will form the subject of a further communication. A. H.

Formation of Closed Chain Compounds from Open Carbon Chains. By W. DIECKMANN (*Ber.*, 27, 102—103).—By the action of sodium on ethylic adipate in molecular proportion at 120°, *ethyl β-ketopentamethylenecarboxylate*, $CH_3 < \begin{matrix} CH_2 \cdot CO \\ CH_2 \cdot CH \cdot COOEt \end{matrix}$, is formed, it yields a green *copper salt*, and produces, in alcoholic solution, a deep blue coloration with ferric chloride. On hydrolysis with dilute sulphuric acid, ketopentamethylene is obtained, and was identified both by its own properties and by those of its oxime. Ethylic

pimelate yields, in a similar manner, *ethyl*ic β -keto-hexamethylenecarboxylate, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CO}- \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{COOEt}$, which may be readily converted into keto-hexamethylene. These results are in complete harmony with v. Baeyer's theory of the formation of closed carbon chains.

J. B. T.

Constitution of Benzene. By A. CLAUS (*J. pr. Chem.*, [2], **48**, 576—595).—A dissertation on the appropriateness of the author's diagonal formula, with special reference to the work of Marckwald (*Abstr.*, 1893, i, 603).

A. G. B.

Reduction by means of Sodium and Alcohol. By A. LADENBURG (*Ber.*, **27**, 78).—Whilst not the originator of this method, the author claims to have been the first to systematically determine the conditions necessary for its advantageous employment, he considers, therefore, that it should bear his name (comp. Einhorn and Willstätter, this vol., i, 87).

J. B. T.

Reduction Products of Benzene. By A. v. BAEYER (*Annalen*, **278**, 88—116).—Berthelot (*Bull. Soc. Chim.*, 1867—68) obtained hexane (b. p. 69°) by heating benzene in a sealed tube at 280° with an excess of fuming hydriodic acid. Baeyer (*Annalen*, **155**, 266) and Wreden (*Annalen*, **187**, 153) confirmed this observation, and found that benzene cannot be reduced by phosphonium iodide at 350°. Kijner (*Abstr.*, 1893, i, 150, 460) observed that the oil obtained by Berthelot's method is a mixture of hexane and hexahydrobenzene, and that when benzene (1 c.c.) is heated with fuming hydriodic acid (25 c.c.) at 260—270°, the product consists entirely of hexahydrobenzene. Independently of the fact that the reduction of benzene appears to give hexane as well as hexahydrobenzene, the process is complicated and costly. For these reasons, the author has employed diketohexamethylene as the starting point for the preparation of the hydrogenised derivatives of benzene. His experiments have been already published to some extent (see *Abstr.*, 1892, 833, 1074; 1893, i, 254).

Diketo-hexamethylene is reduced to quinitol (*Abstr.*, 1892, 833) by sodium amalgam. The product is acetylated and distilled under diminished pressure; the solid *trans*-diacetylquinitol is separated from the *cis*-modification by filtration. The former melts at 102—103°, and the latter at 34—36°. When these acetyl derivatives are boiled with barium hydroxide, *trans*-quinitol, melting at 139°, and *cis*-quinitol, melting at 100—102°, are respectively obtained. They are both colourless crystalline compounds, having a sweet taste at first, which is followed by a bitter one. Their other properties agree with that of the mixture already described (*loc. cit.*). When heated in a sealed tube with fuming hydrobromic acid, the two stereoisomerides yield two *paradibromhexamethylenes*, $\text{C}_6\text{H}_{10}\text{Br}_2$; the *trans*-modification melts at 113°, whilst the *cis*-modification is liquid.

Dihydrobenzene (*Abstr.*, 1892, 1074), when pure, boils at 84—86° (corr.), under a pressure of 718 mm.; the spectroscopic examination of the characteristic blue coloration which it gives with alcoholic

sulphuric acid is described. *Dihydrobenzene tetrabromide* melts at 184—185°.

When quinitol is heated with fuming hydriodic acid in a sealed tube at 100°, *trans-paradiiodohexamethylene*, melting at 144—145°, is obtained, together with the liquid *cis*-modification. *Quinitol iodohydrin* is formed, together with the last-mentioned diiodide, by evaporating a solution of quinitol with dilute hydriodic acid; the crude product, if distilled with quinoline (5 parts), is converted into a mixture of dihydrobenzene and tetrahydrophenol; the latter is a mobile liquid which boils at 166° (corr.) under a pressure of 716 mm., and has the odour of caprylic alcohol, especially when it is warmed with water, which dissolves considerable quantities. It instantaneously reduces permanganate, and behaves towards Bechmann's chromic acid solution (*Annalen*, 250, 325) in the same manner as hydroxyhexamethylene. The *phenylurethane* melts at 79°. *Hydroxyhexamethylene* is obtained when the crude mixture of iodohydrin and diiodide is reduced with glacial acetic acid and zinc dust in the cold; it melts at 16—17°, and boils at 160—161° (corr.) under a pressure of 716 mm. It has the odour of fusel oil, is stable towards cold permanganate, and when warmed with nitric acid is oxidised to adipic acid. The *acetyl* derivative is an oil having the odour of amylic acetate, which boils at 175—177° (corr.) under a pressure of 720 mm. The *phenylurethane* melts at 80—81°. When hydroxyhexamethylene is treated with Bechmann's reagent (*loc. cit.*), it yields keto-hexamethylene, identical with that obtained by distilling calcium pimelate (Mager, *Abstr.*, 1893, 558), and with that prepared by Drechsel, by electrolysis of phenol with alternating currents (*Abstr.*, 1888, 1277). It boils at 155—156° (corr.) under a pressure of 716 mm., has the odour of peppermint, and its sp. gr. at about 21° is 0.952; the pure compound gives no coloration with Millon's reagent. The *oxime* melts at 88°. When the ketone is heated with ammonium formate in a sealed tube at 190—200°, or when the oxime is reduced with sodium and alcohol, *hexamethylenamine* is obtained. It is a colourless liquid, having an odour resembling that of conine; the *hydrochloride* melts at 204°; the *aurochloride* at 190—191°. The *acetyl* derivative melts at 104°, the *benzoyl* derivative at 147°, the *phenylureide* at 180°, and the *phenylthiureide* at 147—148°.

Keto-hexamethylene forms a phenylhydrazone melting at 74—77° with decomposition, which, when warmed with mineral acids, yields Graebe and Glaser's hydrocarbazole; it melts at 114° (not 120°). Hydroxyhexamethylene is obtained when keto-hexamethylene is reduced with sodium and moist ether. If the hydroxy-compound is heated with fuming hydrobromic or hydriodic acid, *bromhexamethylene*, boiling at 165—166° (corr.) under a pressure of 714 mm., and *iodohexamethylene*, boiling at 180°, are respectively produced.

When bromhexamethylene is warmed with quinoline (5 parts), *tetrahydrobenzene*, boiling at 82—84° under a pressure of 715 mm. (see also *Abstr.*, 1893, i, 255), is obtained. The *tribromide* boils at 215—220°, with slight decomposition; the nitrosate, $\text{NO} \cdot \text{C}_6\text{H}_{10} \cdot \text{ONO}_2$, forms white needles and melts at 150° with decomposition, and the *nitrosite*, $\text{NO} \cdot \text{C}_6\text{H}_{10} \cdot \text{ONO}$, also melts at about 150° with decomposition.

Hexamethylene (hexahydrobenzene) is obtained by reducing iodhexamethylene with zinc dust and acetic acid in the cold. The crude product is freed from unsaturated compounds by shaking it with cold, aqueous, 3 per cent. permanganate; it has a petroleum-like odour, and boils at 79—79.5° (corr.) under a pressure of 718 mm.

The paper concludes with a general discussion of the results obtained up to the present. So far as our present knowledge extends, the derivatives mentioned in the first column of the following table may be regarded as the parent compounds of those in the second.

Dihydrobenzene,	Terpene,
Tetrahydrobenzene,	Menthene,
Hexahydrobenzene,	Hexahydrocymene,
Quinitol,	Terpinol,
Tetrahydrophenol,	Terpineol,
Hexahydrophenol,	Menthol,
Ketohexamethylene.	Menthone.

The values given in the following table are approximate.

	Increase in heat of combustion.	Increase or decrease in boiling point.
Benzene to dihydrobenzene.....	68.2 cal.	+ 5.0°
Dihydro- to tetrahydro-benzene..	44.0 „	— 2.5
Tetrahydro- to hexahydro-benzene	41.2 „	— 3.5
Hexahydrobenzene to hexane	58.0 „	— 10.0
		A. R. L.

Action of Water on Tribromotrinitrobenzene and on Tribromodinitrobenzene. By C. L. JACKSON and W. H. WARREN (*Amer. Chem. J.*, 16, 28—35; compare Abstr., 1892, 1182).—Symmetrical tribromotrinitrobenzene (m. p. 285°) is converted on boiling with sodium carbonate and water into a mixture of the sodium salts of trinitrophenol and a new *tribromodinitrophenol*,



The latter crystallises from dilute alcohol in pale, yellow, square-ended needles, is readily dissolved by most of the ordinary solvents, forms a characteristic barium salt, and melts at 194°. Tribromodinitrobenzene (m. p. 192°) prepared from symmetrical tribromobenzene gives, under the same conditions, a dibromodinitrophenol, which melts at 147—148°, a temperature almost identical with that (146—146.5°) of the only other known dibromodinitrophenol, which has been recently described by Garzino (*Atti. R. Accad. Sci. Torino*, 25, 263), and is obtained by the action of nitric acid on the propionic derivative of metabromophenol. The identity, however, is only apparent, as Garzino's compound gives barium and potassium salts differing markedly from the salts of the new compound. Mixed with the dibromodinitrophenol above described is an oily phenol, which was not obtained in a pure state.

Tribromotrinitrobenzene and tribromodinitrobenzene are, therefore, decomposed by water and sodium carbonate in the same general

manner as with sodium ethoxide, the trinitro-compound in both cases showing two parallel reactions, in one of which nitro-groups, in the other bromine atoms, are removed, whilst the dinitro-compound in both cases loses part of its bromine. It is to be noted, however, that whilst the ethoxide removes two nitro-groups from the trinitro-, and two bromine atoms from the dinitro-compound, water in each of these cases removes only one, although, like the ethoxide, it removes all three of the bromine atoms from the tribromotrinitrobenzene.

The constitution of the new tribromodinitrophenol can be only $\text{Br}_3 : (\text{NO}_2)_2 = 2 : 4 : 6 : 3 : 5$, as the substance from which it is derived is symmetrical. The dibromodinitrophenol, on the other hand, can be either $\text{OH} : \text{Br}_2 : (\text{NO}_2)_2 = 1 : 3 : 5 : 2 : 4$, or $= 1 : 3 : 5 : 2 : 6$, but which it is has not yet been determined. G. T. M.

New Class of Compounds resulting from the Action of Iodine in Presence of Alkali on Phenols. By T. R. CAESWELL (*Chem. News*, 68, 87—89, 99—101, 131—132, 153—155, 166—167, 181—183, 195—196, 203, 214—216, 227—228).—The author refers to the researches of Messinger (*Abstr.*, 1887; 1150, *et seq.*). He states that he has obtained several new derivatives by the action of iodine in presence of alkali on various phenolic compounds, and gives analytical data. A. R. L.

Dihydroresorcinol. By G. MEHLING (*Annalen*, 278, 20—57).—*Dihydroresorcinol*, $\text{C}_6\text{H}_8\text{O}_2$, is obtained when 2 per cent. sodium amalgam (5 kilos.) is gradually added to a solution of resorcinol (100 grams) in water (1 litre) at 90° , a current of carbonic anhydride being passed through the solution meanwhile; the alkaline liquid is acidified with dilute sulphuric acid, filtered, and the filtrate extracted with ether. After distilling off the ether, the compound remains as a syrup which, on being cooled, solidifies; the crystals are washed with anhydrous ether. It crystallises from benzene in colourless, lustrous prisms, and melts at $104\text{--}106^\circ$ with loss of water and formation of the compound, $\text{C}_{12}\text{H}_{14}\text{O}_2$; the aqueous solution has an acid reaction, decolorises permanganate, gives an intense violet-red coloration with ferric chloride, and reduces ammoniacal silver solution, but not Fehling's solution. The sodium, barium, and calcium salts were prepared; the silver salt, $\text{C}_6\text{H}_7\text{O}_2\text{Ag}$, crystallises from hot water in grey, lustrous needles. Dihydroresorcinol forms condensation compounds with aldehydes; that obtained from formaldehyde has the formula $\text{CH}_2(\text{C}_6\text{H}_7\text{O}_2)_2$, and melts at $132\text{--}133^\circ$.

Glutaric and succinic acids are formed when dihydroresorcinol is oxidised with alkaline permanganate. The production of glutaric acid explains the structure of dihydroresorcinol, whilst a consideration of the facts described below indicates that it is a tautomeric compound thus, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 & \text{---} & \text{CO} \\ \text{CH}_2 & \cdot & \text{C}(\text{OH}) \end{smallmatrix} > \text{CH}$ or $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{CH}_2$.

The dioxime, $\text{C}_6\text{H}_8(\text{NOH})_2 + 2\text{H}_2\text{O}$, is rendered anhydrous when kept over concentrated sulphuric acid, and then melts at $154\text{--}157^\circ$, decomposing at about 200° ; it reduces Fehling's solution when boiled with it. *Metadiamidohexamethylene*, $\text{C}_6\text{H}_{10}(\text{NH}_2)_2$, is obtained by re-

ducing the dioxime with sodium and boiling alcohol; it is a colourless oil which fumes slightly in the air, mixes in all proportions with water, is soluble in anhydrous, but not in moist ether, boils at 193° (752 mm.), and its sp. gr. at 15° is 0.956. The *platinochloride* melts with decomposition at 255° , and the *diacetyl* derivative forms colourless needles, and melts at 256° .

Dihydroresorcinol phenylhydrazine, $C_6H_5O:N:NPh$, is precipitated on adding aqueous phenylhydrazine to a solution of dihydroresorcinol; it crystallises in colourless needles, melts at $176-177^{\circ}$, and reduces Fehling's solution when boiled with it. If a solution of dihydroresorcinol is gently heated with an excess of phenylhydrazine, the *azo*-compound, $NHPh:N:C_6H_7:N:NPh$, is obtained; it crystallises from alcohol in garnet-red prisms.

Chlorotetrahydroresorcinol, $CH_2<\begin{smallmatrix} CH_2- & CO \\ CH_2 & CH(OH) \end{smallmatrix}>CHCl$, separates as a colourless, crystalline powder when hydrogen chloride is passed into a solution of dihydroresorcinol in chloroform; it is stable towards air, readily dissolves in water, forming dihydroresorcinol, but is almost insoluble in ether, chloroform, and benzene. If a solution of dihydroresorcinol in chloroform is treated with bromine in the cold, *dibromotetrahydroresorcinol* is obtained. It is a highly unstable compound, readily losing hydrogen bromide when boiled with water, *bromodihydroresorcinol*, $CH_2<\begin{smallmatrix} CH_2- & CO \\ CH_2 & C(OH) \end{smallmatrix}>CBr$, separating from the aqueous solution on cooling; this melts at 166° with evolution of hydrogen bromide, decomposes solutions of alkali carbonates, reacts with phenylhydrazine in the same manner as dihydroresorcinol, but appears not to form an oxime. It does not unite with bromine, but, when treated with the latter, *bromoresorcinol*, $C_6H_3Br(OH)_2$, is formed; when heated with phthalic anhydride (5 parts) fluorescein is obtained.

When the silver salt of dihydroresorcinol is treated with alkylic iodides or bromides, alkyl derivatives, $CH_2<\begin{smallmatrix} CH_2- & CO \\ CH_2 & C(OR') \end{smallmatrix}>CH$, are produced; they are colourless oils, devoid of odour, the *methyl* derivative being soluble in water, whilst the *ethyl* and *allyl* derivatives are insoluble in water. They are all decomposed by water into the alcohol and dihydroresorcinol, the more readily in presence of hydroxylamine; hence attempts to prepare oximes were unsuccessful. Monacetyl and monobenzoyl derivatives (not di-derivatives) can be prepared, but they are even more unstable towards water than the last-mentioned alkyl derivatives. Dihydroresorcinol dissolves in acetic chloride, forming chlorotetrahydroresorcinol (see above).

Dihydroresorcinol dicyanhydrin, $CH_2<\begin{smallmatrix} CH_2 \cdot C(OH)(CN) \\ CH_2 \cdot C(OH)(CN) \end{smallmatrix}>CH_2$, is obtained by adding hydrochloric acid to an intimate mixture of dihydroresorcinol and potassium cyanide cooled by ice, dissolving the product in a small quantity of water, and extracting with ether. It dissociates in 2 per cent. aqueous solution into dihydroresorcinol and hydrogen cyanide, and when the latter is removed by a continuous current of air, the dissociation is practically complete after some

hours. The compound dissolves in hydrochloric acid of sp. gr. 1.19, but the temperature soon rises; if care is taken not to allow it to exceed 45°, a magma is obtained consisting of ammonium chloride and *dihydroxyhexahydroisophthalimide*, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{C}(\text{OH}) \\ \text{CH}_2 \cdot \text{C}(\text{OH}) \end{smallmatrix} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{NH}$;

the latter crystallises from boiling water in lustrous prisms, melts at 272—273° with evolution of gas, and is readily soluble in alkalis.

Dihydroxyhexahydroisophthalic acid, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{C}(\text{OH})(\text{COOH}) \\ \text{CH}_2 \cdot \text{C}(\text{OH})(\text{COOH}) \end{smallmatrix} > \text{CH}_2$,

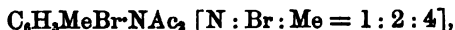
is formed when the last compound is boiled for a short time with hydrochloric acid; it crystallises in delicate needles or lustrous prisms, melts at 217—218° with evolution of gas, is sparingly soluble in cold water, and as good as insoluble in alcohol and ether. The *barium* salt crystallises with 4H₂O; if it is boiled with dilute sulphuric acid and the filtrate evaporated, *dihydroxyhexahydroisophthalic anhydride* is obtained; this crystallises from glacial acetic acid in lustrous prisms, melts at 174—176°, and is readily soluble in water. When *dihydroxyhexahydroisophthalimide* is heated with zinc dust, pyrroline, ammonia and indifferent compounds are formed, whilst if it is boiled with sodium and amyl alcohol, an oily base, not miscible with water, is obtained, together with piperidine.

A. R. L.

Oxidation of Amido-Bases by Sodium Peroxide. By O. FISCHER and J. TROST (*Ber.*, 26, 3083—3085).—The oxidation of amido-bases with sodium peroxide proceeds in a different manner in acid and in alkaline solution; in the former case, the products are usually of a complicated nature, whilst in alkaline solution the amido-group is converted into the nitro-group. Thus, aniline in this manner yields nitrobenzene, and the phenylenediamines are all converted into the corresponding nitranilines. Orthoparatoluylenediamine differs from these, inasmuch as, by the action of an excess of sodium peroxide, both amido-groups may be converted into nitro-groups.

H. G. O.

Diacetyl-derivatives of certain Aromatic Amines. By F. ULFFERS and A. v. JANSON (*Ber.*, 27, 93—101).—The following compounds have been prepared in order to ascertain the relative facility with which the acetyl derivatives of certain amines are formed, and also the influence of substituting groups on the reaction. *Diacetyl-bromaniline*, $\text{C}_6\text{H}_4\text{Br} \cdot \text{N}(\text{Ac})_2$ [1 : 4], is prepared by heating acetylparabromaniline with acetic anhydride for eight hours at 205—210°, and crystallises from light petroleum in aggregates of needles or prisms, melting at 74—74.5°. *Diacetylbromotoluidine*,



is prepared from the acetyl derivative at 150—160°, and crystallises in large, flat prisms, which melt at 75—75.5°. *Diacetyldibromaniline*, $\text{C}_6\text{H}_3\text{Br}_2 \cdot \text{N}(\text{Ac})_2$ [N : Br : Br = 1 : 2 : 4], is formed from the acetyl com-

pound by heating for 6 hours at 200° ; it crystallises in hard plates and melts at $54-55^{\circ}$. *Acetyldibromotoluidine*, $C_6H_2Br_2Me \cdot NHAc$ [$N : Br : Br : Me = 1 : 2 : 6 : 4$], is formed at 100° and crystallises in large flat prisms, melting at $199-200^{\circ}$. The *diacetyl derivative* is deposited in thick plates or prisms melting at $101-101.5^{\circ}$. *Diacetyl-tribromaniline*, $C_6H_2Br_3 \cdot NAc$, [$N : Br : Br : Br = 1 : 2 : 4 : 6$], melts at $127-128^{\circ}$ instead of 123° as stated by Remmers. *Diacetylnitrobromotoluidine*, $NO_2 \cdot C_6H_2MeBr \cdot NAc$, [$N : Br : Me : NO_2 = 1 : 2 : 4 : 6$], crystallises in large, pale, greenish-yellow prisms, melting at 79° .

The following compounds were all prepared by heating the amine (1 mol.) with acetic anhydride (6-7 mol.) for 10 hours at 200° , in order to ascertain the relative quantities formed. The yields are given in per cent. of the theoretical. *Diacetylnitraniline*, [$NAc : NO_2 = 1 : 4$], crystallises in large, flat, pale-yellow plates, and melts at $128.5-129^{\circ}$. The yield is 15-20 per cent. *Diacetylnitrotoluidine*, [$N : NO_2 : Me = 1 : 2 : 4$] forms lemon-yellow prisms, melting at 78° . The yield is 30-35 per cent. *Diacetyldinitraniline*, [$NAc : (NO_2)_2 = 1 : 2 : 4$], is deposited in pale-yellow crystals and melts at $112-113^{\circ}$. The yield is about 20 per cent. *Diacetyldinitrotoluidine*, [$NAc : (NO_2)_2 : Me = 1 : 2 : 6 : 4$] crystallises in thick, lemon-yellow plates, and melts at 129.5° . The yield is 70-80 per cent. The above results show that the monacetyl derivatives are first formed and are then converted into the diacetyl compounds, but the reaction is influenced by the nature, number, and position of the substituting groups. The brominated amines react much more readily than the corresponding nitroamines; an increase in the number of bromine-atoms or nitro-groups retards the entrance of the acetyl-groups. Diacetyl derivatives are formed with greater difficulty than monacetyl compounds; the presence of negative groups generally hinders the reaction, especially in the para-position, but in the ortho-position relative to the amido-group, they facilitate the formation of acetyl derivatives.

J. B. T.

Trianilidodinitrobenzene and Related Compounds. By C. L. JACKSON and H. N. HERMAN (*Amer. Chem. J.*, 16, 35-43; compare Abstr., 1890, 497; 1892, 1217).—Numerous attempts to prepare a second modification of trianilidotrinetrobenzene, or of ethylic anilidotrinetrophenylmalonate have, without exception, led to negative results, as no change of the full yellow colour or the crystalline form of either of these substances could be observed. This result is remarkable in view of the occurrence of two modifications of trianilidodinitrobenzene and of ethylic anilidotrinetrophenyltartronate.

When trianilidodinitrobenzene is crystallised from a mixture of benzene and alcohol, it appears in two forms; one, the nearly square prisms of an orange colour, like that of potassium dichromate, already described (*loc. cit.*); the other, yellow, like potassium chromate, in bladed crystals, or plates looking like flattened monoclinic prisms, terminated by two planes, or, less commonly, with square ends, which, when the cooling takes place rapidly, appear in circular groups of little needles. These two varieties, differing so widely in physical form and colour, melt at the same temperature, 179° , the yellow

modification previously becoming orange-coloured at 140° . The yellow variety is obtained by crystallisation of the substance from a solvent containing a relatively large proportion of benzene; it cannot, however, be completely freed from admixture with the orange-red crystals, which are the sole product of recrystallisation from a solvent containing very little benzene. That the two varieties are not polymeric is shown by their producing the same depression in the freezing point of a benzene solution. The numbers obtained in both cases agree closely with that required for a molecular weight corresponding with the formula $C_6H(NHPh)_3(NO_2)_3$. In all probability the two modifications are physical isomerides, or perhaps the substance is dimorphous.

Trianilidodinitrobenzene forms a remarkable additive product with chloroform, $C_6H(NHPh)_3(NO_2)_2 \cdot CHCl_3$, which is readily obtained on allowing a solution of the nitro-compound in chloroform and alcohol to evaporate at temperatures between 50° and 70° . It crystallises in well-characterised prisms, of a dark brownish-red colour, not unlike that of potassium ferricyanide, and loses part of its chloroform at ordinary temperatures, but is not completely freed from it until heated to 100° .

Triparatoluidodinitrobenzene, $C_6H(NH \cdot C_7H_7)_3(NO_2)_2$, melts at 197° , and forms an additive product with chloroform very similar to that above described. It crystallises in brownish-red plates and in yellow, thread-like, felted crystals, the latter becoming red at 180° , and also melting at 197° .

Triorthotoluidodinitrobenzene crystallises in red, stout-pointed needles, melts at 243° , and does not appear to exist in two modifications.

G. T. M.

Bromine Derivatives of Metaphenylenediamine. By C. L. JACKSON and S. CALVERT (*Ber.*, 27, 20).—The authors have obtained the tribromophenylenediamine, melting at 157° , which has been described by Vaubel (*Abstr.*, 1893, i, 560), by the action of the calculated amount of bromine on a solution of the hydrochloride of metaphenylenediamine, or a mixture of the free base and water. *Diacetyltribromophenylenediamine*, $C_6HBr_3(NHAc)_2$, melts above 330° . Metaphenylenediacetamide when treated with bromine only, takes up two atoms of bromine, forming *diacetyldibromometaphenylenediamine*, which melts at 260° . The corresponding *diamine* melts at 136° .

A. H.

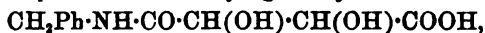
Diacetanilide. By A. BISTRZYCKI and F. ULFFERS (*Ber.*, 27, 91—93).—Diacetanilide is prepared by heating acetanilide (1 mol.) with acetic anhydride (2 mol.) in a sealed tube for 8—10 hours at 200 — 205° . The yield is 90 per cent. of the theoretical. The properties of the compound agree with the description given by Kay (this vol., i, 76). The physiological properties of diacetanilide are in every way identical with those of acetanilide.

J. B. T.

Tartaric and Citric Derivatives of Benzylamine. By E. GIUSTINIANI (*L'Orosi*, 16, 253—258; compare *Abstr.*, 1893, i, 264).—

Benzyltartarimide, $CH_2Ph \cdot N < \begin{array}{c} CO \cdot CH \cdot OH \\ | \\ CO \cdot CH \cdot OH \end{array}$, is extracted by boiling

water from the product obtained on heating tartaric acid with benzylamine at 165°; it forms white, crystalline laminæ melting at 196°, is very soluble in alcohol or acetic acid, and gives an oily *nitro-derivative* when treated with fuming nitric acid. On dissolving the imide in concentrated potash and acidifying, *benzyltartramic acid*,



separates; it crystallises in thin, white needles melting at 166°, and is readily reconverted into the imide by hot, dilute hydrochloric acid. The *barium* salt forms lustrous, white crystals containing H_2O , which is given off in a vacuum or at 100°. Both the acid and the imide yield acetyl and benzoyl derivatives.

Benzylamine citrate crystallises in long needles which contain water, melts at 110°, and on heating at 155°, yields *monobenzylcitrimide*, $\text{C}_6\text{H}_5\text{O}_2\text{C}(\text{CO})\text{N}\cdot\text{CH}_2\text{Ph}$; this is very soluble in alcohol, and crystallises in yellowish laminæ, which soften at 189°, and melt at 197°; it gives off benzylamine on heating with caustic alkali, and also yields an *acetyl* derivative. On gently warming the imide with aqueous ammonia, and decomposing the cooled solution with acetic acid, *monobenzylcitramic acid*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5\text{O}_2\cdot\text{COOH}$, is deposited; it is best prepared by dissolving the imide in baryta solution, and precipitating with the exact quantity of sulphuric acid. It forms colourless leaflets melting at 165° with decomposition, and is soluble in water, alcohol, or ether. The *barium* salt forms small, lamellar crystals containing $2\text{H}_2\text{O}$, which is lost at 100°.

Monobenzylaconitrimide (?) sublimes in yellowish needles on heating benzylcitrimide at 230° in a current of carbonic anhydride; it combines with bromine to give an oily compound, which easily loses hydrogen bromide, yielding *monobrombenzylcitraconimide* (?),



W. J. P.

Isobutenylphenylamidine. By O. HINSBERG and F. FUNCKE (*Ber.*, 26, 3092—3094).—From the result of his investigations, Hinsberg concluded many years ago that the orthodiamines and aldehydes always interact with formation of anhydro-bases, and, with one exception, subsequent investigation has confirmed the rule. Lassar-Cohn, however (Abstr., 1890, 138), by the action of isobutyraldehyde on orthodiamidobenzene, obtained a substance to which he ascribed the formula $\text{C}_{10}\text{H}_{14}\text{N}_2$, and containing, therefore, 2 atoms of hydrogen more than the anhydro-base, isobutenylphenylamidine, $\text{C}_6\text{H}_4\langle\text{N}\rangle\text{NH}\text{CPr}^s$. The authors have, therefore, reinvestigated this reaction, and find that the anhydro-base is in reality formed, and that Lassar-Cohn's statement is incorrect.

The compound described by Griess as gluco-orthodiamidobenzene (Abstr., 1887, 475, 930) is, according to the authors, in all probability also an anhydro-base.

H. G. C.

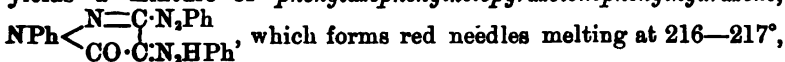
Action of Diazobenzene on Acetaldehyde, Pyruvic acid, and the Hydrazone of the latter. By E. BAMBERGER and J. MÜLLER

(Ber., 27, 147—155).—In alkaline solution, diazobenzene reacts with acetaldehyde, forming phenylazoformazyl, $C(N,Ph)_2 \cdot N_2HPh$, together with formic acid and water; phenylazoformazyl is best prepared in this way. It yields explosive metallic derivatives, and a yellow *acetyl derivative* melting at about 190° .

With pyruvic acid, *formazylglyoxalic acid*,



is the chief product, but some phenylazoformazyl and oxalic acid are also formed; these can be shown to be produced by the action of diazobenzene on formazylglyoxylic acid. This acid forms red needles melting at 166° ; it yields explosive, metallic derivatives, also a *methylic salt* in red needles melting at 124 — 125° , and an *ethylic salt* as red plates or cubes melting at 105 — 106° . With acetic anhydride and zinc chloride, it does not yield an acetyl derivative, but is transformed into an isomeric substance, which crystallises in yellow needles, and melts at 158 — 163° . Its *phenylhydrazone* is a dark brown powder, and, when heated in acetic acid solution, it yields a mixture of *phenylazophenylketopyrazolonephenylhydrazone*,



and *phenylazophenylsotriazolecarboxylic acid*, $NPh \cdot \begin{array}{c} N:C \cdot N,Ph \\ | \\ N:C \cdot COOH \end{array}$, which crystallises in orange-yellow plates melting at 195 — 196° , and yields metallic salts, often explosive. Formazylglyoxalic acid is, finally, converted by boiling hydrochloric acid into phenazine,



With pyruvic acid hydrazone, diazobenzene, in alkaline solution, yields *methylformazyl*, $N_2Ph \cdot CMe \cdot N_2HPh$, a substance which forms long, orange needles melting at 120 — 121° , and, unlike hydrogen formazyl, is easily oxidisable. It appears also to be formed when alkaline diazobenzene reacts with methylacetoacetic acid. C. F. B.

Action of Diazobenzene on Nitromethane. By E. BAMBERGER (Ber., 27, 155—160).—The product of the reaction, when the latter is carried out in alkaline solution, is not “azonitromethylphenyl,” as Frieser thought (Abstr., 1876, i, 85), but *nitroformazyl*,



It exhibits all the properties of formazyl compounds, and has in addition strong acid properties. Further, when heated with alkaline diazobenzene, it yields phenylformazyl, $N_2Ph \cdot CPh \cdot N_2HPh$.

The compound that Frieser was looking for, and which is probably not an azo-compound, but a hydrazone—nitroformaldehydehydrazone, $NO_2 \cdot CH \cdot N_2HPh$, can be obtained, together with some nitroformazyl, by allowing diazobenzene to react with potassium-nitromethane in a slightly acid solution. It crystallises in yellow needles melting at 84 — 85° , and yields a silver derivative. C. F. B.

Action of Diazobenzene on Acetonecarboxylic acid. By H. v. PECHMANN and L. VANINO (*Ber.*, 27, 219—224).—Since it has been shown that diazobenzene yields, with certain fatty derivatives, not azo-, but hydrazo-compounds, a different constitution must be assigned to the substances described in *Abstr.*, 1892, 161. The “disbenzeneazoacetone,” there described as obtained by the action of diazobenzene on acetonecarboxylic acid, is really *propanon-diphenylhydrazone*, $\text{CO}(\text{CH}:\text{N}_2\text{HPh})_2$, as it is shown by the fact that its diacetyl derivative yields acetanilide when treated with alkalis, from which it follows that the acetyl group must be attached to the nitrogen atom, and, consequently, that the original compound is a hydrazone, and not an azo-compound. This *diacetyl derivative*, $\text{CO}(\text{CH}:\text{N}_2\text{AcPh})_2$, forms lemon-yellow needles melting, with decomposition, at 167—168°. *Propanon-diparatolylhydrazone*,



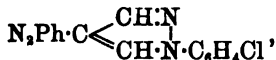
is obtained from acetonedicarboxylic acid and paradiazotoluene, and forms red needles melting, with decomposition, at 192—193°. *Propanon-diparachlorophenylhydrazone*, $\text{CO}(\text{CH}:\text{N}_2\text{H}\cdot\text{C}_6\text{H}_4\text{Cl})_2$, from the same acid with parachlorodiazobenzene, forms red needles shot with violet, and melts at 191°.

Propanetriphenylhydrazone, $\text{N}_2\text{HPh}\cdot\text{C}(\text{CH}:\text{N}_2\text{HPh})$, is the correct name of the substance obtained by the action of phenylhydrazine on disbenzeneazoacetone, and previously described as the hydrazone of the latter. *Propane-1:2-diphenyl-3-methylphenylhydrazone*,



is obtained by the action of methylphenylhydrazone; it forms lemon-yellow needles melting at 192—193°.

The substance formed when propanetriphenylhydrazone is boiled with acetic anhydride is now shown to be, not $\text{C}_{22}\text{H}_{20}\text{N}_6$, but 1-phenyl-4-benzeneazopyrazole, $\text{N}_2\text{Ph}\cdot\text{C} \begin{smallmatrix} \text{CH}:\text{N} \\ \text{CH}:\text{NPh} \end{smallmatrix}$. The diphenylmethylphenylhydrazone forms no such compound, but the diparachlorophenylhydrazone, when heated with phenylhydrazine and glacial acetic acid, yields 1-parachlorophenyl-4-benzeneazopyrazole,

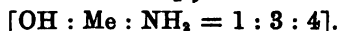


as yellow plates melting at 152°. *Acetylparachlorophenylhydrazone* is formed at the same time, and was obtained in colourless needles melting at 154°. C. F. B.

Decomposition of Substituted Diazobenzenenimides. By P. FRIEDLÄNDER and M. ZEITLIN (*Ber.*, 27, 192—198).—It has long been known that diazobenzenenimides, when warmed with more or less dilute sulphuric acid, yield para- (or ortho-) amidophenols. The authors think that hydroxylamines are formed as an intermediate stage, for example, $\text{C}_6\text{H}_4\cdot\text{N}_2 + \text{H}_2\text{O} = \text{N}_2 + \text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and they attempted to isolate these by examining diazobenzenimides in which the para-position was already occupied. They were not

successful, however, for a simple reaction does not take place, except in the case of *nitrodiazobenzenimides*, which readily yield *nitramidophenols*, but even then no intermediate product could be isolated. In the solitary case of *nitrotolyldiazimide* [$\text{Me} : \text{NO}_2 : \text{N} = 1 : 2 : 4$], a solution was obtained which contained no *nitramidocresol*, but yielded *metatolylenediamine* when reduced; probably this solution contained *nitrotolylhydroxylamine*, but attempts to isolate the latter yielded only amorphous polymerisation products.

Tolyldiazimide [$\text{Me} : \text{N}_2 = 3 : 4$] yields *amidocresol*,



Orthonitrodiazobenzenimide [$\text{NO}_2 : \text{N}_2 = 3 : 4$] yields the *nitramidophenol* [$\text{NO}_2 : \text{NH}_2 : \text{OH} = 3 : 4 : 5$], which crystallises in small, red needles melting at $135\text{--}136^\circ$, yields a *monacetyl derivative* as yellowish-red needles, and, in alcoholic solution, is converted by nitrous acid into 3 : 5-nitrophenol. *Paranitrodiazobenzenimide* [$\text{NO}_2 : \text{N}_2 = 1 : 4$] yields the *nitramidophenol* [$\text{NO}_2 : \text{NH}_2 : \text{OH} = 1 : 4 : 5$] as light brown needles melting at $201\text{--}202^\circ$, convertible into 1 : 5-nitrophenol. *Metanitrodiazobenzenimide* [$\text{NO}_2 : \text{N}_2 = 2 : 4$] yields the *nitramidophenol* [$\text{OH} : \text{NO}_2 : \text{NH}_2 = 1 : 2 : 4$], which forms reddish needles melting at $126\text{--}128^\circ$, yields a *monacetyl derivative* as yellow needles melting at $157\text{--}158^\circ$, and is convertible into 1 : 2-nitrophenol.

C. F. B.

Benzenylamidoxime. By E. BAMBERGER (*Ber.*, 27, 160—163).—An attempt was made to prepare an *amidrazone*, $\text{NH}_2 \cdot \text{CPh} \cdot \text{N} \cdot \text{HPh}$, by the action of phenylhydrazine in acetic acid solution on *benzenylamidoxime*, $\text{NH}_2 \cdot \text{CPh} \cdot \text{NOH}$, but the product of the reaction was found to be a mixture of *phenylformazyl*, $\text{N}_2 \cdot \text{Ph} \cdot \text{CPh} \cdot \text{N} \cdot \text{HPh}$, and *benzoylphenylhydrazine*, $\text{CPhO} \cdot \text{N} \cdot \text{H}_2 \cdot \text{Ph}$.

C. F. B.

Isomerism of Derivatives of Chloroquinonemeta-oxime. By F. KEHRMANN (*Ber.*, 27, 217—219).—Bridge (this vol., i, 25) is in error in supposing that the two benzoates and the two methylic ethers of *chloroquinoneoxime* are structurally isomeric. Their isomerism is geometrical only, for they are all derived from the same *chloroquinone-oxime* [$\text{O} : \text{Cl} : \text{NOH} = 1 : 2 : 4$], as is shown by the fact that both benzoates are oxidised by nitric acid to the same *dinitrochlorophenol* [$\text{OH} : \text{Cl} : (\text{NO}_2)_2 = 1 : 2 : 4 : 6$], and, like the two methylic ethers, are both reduced by stannous chloride to the same *chloramidophenol* [$\text{OH} : \text{Cl} : \text{NH}_2 = 1 : 2 : 4$]. It is not a case of tautomerism, nor is the isomerism of the kind existing between a “nitrogen-” and an “oxygen-ether,” for both the methylic ethers are obtained by the action of *methoxylamine* on *chloroquinone*; either of these ethers can, by heating, be partially converted into its isomeride.

C. F. B.

Auramines. By A. STOCK (*J. pr. Chem.*, [2], 48, 601).—The author has already stated (*Abstr.*, 1893, i, 472) that the di-substituted *auramines* are decomposed by aqueous ammonia, partly into amines and ketones, and partly with the formation of non-substituted *auramines*. He now points out that the concentration of the solution has considerable influence on the change; the greater this is, the more does the formation of an *auramine* become the main reaction.

A. G. B.

Action of Phosphorus Pentachloride on Urethanes. By F. LENGFELD and J. STIEGLITZ (*Amer. Chem. J.*, 16, 70—78; compare Abstr., 1893, i, 310 and 631).—On heating phosphorus pentachloride with phenylurethane at 55°, ethylic chloride is slowly evolved, and chloroformanilide, which melts at 53—55°, and decomposes at 90—100°, is obtained (compare Hentschel, Abstr., 1885, 888). Phenylurethane first gives rise to the compound $\text{NPh}\cdot\text{CCl}_2\cdot\text{OEt}$, which loses ethylic chloride, giving $\text{HNPh}\cdot\text{COCl}$. This result is noteworthy, since hydrochloric acid is apparently eliminated from the chloramides more easily than alkyl chlorides from dichloroglycollic ethers.

G. T. M.

Isomerism in the Quinazoline Series. By C. PAAL and J. WEIL (*Ber.*, 27, 34—47).—Söderbaum and Widman (Abstr., 1889, 972; 1890, 178) on the one hand, and Busch (this vol. i, 146) on the other, have described a number of derivatives of keto- and thio-tetrahydroquinazolines to which identical formulæ have been ascribed by these authors, but which differ in properties. The substance described by Paal and Bodewig (Abstr., 1891, 943) as phenylketotetrahydroquinazoline, differs from the compounds prepared by the above-named chemists and known by the same name. The authors have, therefore, re-examined the substance obtained by Paal and Bodewig, which was prepared by the reduction of orthonitrobenzyl-diphenylcarbamide by tin and hydrochloric acid. The compound obtained in this manner, or by reduction of the nitro-carbamide with zinc dust and acetic acid at a low temperature, proves, however, to be *orthamidobenzyl-diphenylcarbamide*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{CO}\cdot\text{NPh}$, and not phenylketotetrahydroquinazoline. This does not appear from the analysis of the substance, the composition of the two compounds being too nearly alike to permit of a distinction by this means, but from a determination of the molecular weight by the freezing point method and from the general behaviour of the substance. It crystallises in white needles, and, when quite pure, melts at 177°. When treated with alkaline permanganate, it is almost completely decomposed, whereas the two phenylketoquinazolines are thereby converted into the same diketo-compound. Nitrous acid converts it into a substance of acid properties, which is probably orthohydroxybenzyl-diphenylcarbamide. When boiled with acetic anhydride, it is converted into orthacetamidobenzylacetanilide. When orthamidobenzyl-diphenylcarbamide is heated for a short time above its melting point, it decomposes with elimination of aniline and formation of phenylketotetrahydroquinazoline, identical in every respect with the substance melting at 186—188°, described by Busch.

The *hydrochloride* of orthamidobenzyl-diphenylcarbamide is a white, crystalline powder, which is moderately soluble in water and alcohol, and melts at 143—144°.

Orthanilidobenzylphenylcarbamide, $\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NPh}$, is formed by the combination of phenylcarbimide with orthamidobenzylaniline in benzene solution. It crystallises in white, spherical masses or colourless needles melting at about 102°. When heated above its melting point, it decomposes into aniline and the phenylketo-tetrahydroquinazoline, melting at 186—188°, described by Busch.

Orthonitrobenzylparatolylphenylcarbamide,

is prepared by the addition of phenylcarbimide to orthonitrobenzylparatoluidine in benzene solution. It crystallises in light-yellow, lustrous plates melting at 119° , and is readily soluble in benzene and chloroform, less readily in alcohol. On reduction with zinc dust and acetic acid, it is converted into *orthamidobenzylparatolylphenylcarbamide*, which is readily soluble in ether, alcohol, &c., and crystallises in druses of white needles melting at 129° . It forms crystalline salts with dilute mineral acids, and yields an acetyl compound melting at 185° .

When it is heated above its melting point, it decomposes into aniline and the paratolylketotetrahydroquinazoline of melting point $218\text{--}220^\circ$, described by Busch. A. H.

Action of Phthalic Anhydride on Paramidophenol and the corresponding Ethers. By E. CASTELLANETA (*L'Orosi*, 16, 289—

298).—*Paramethoxyphenylphthalimide*, $\text{C}_6\text{H}_4\langle\frac{\text{CO}}{\text{CO}}\rangle\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is prepared by heating phthalic anhydride with paramidoanethoil hydrochloride at 190° or phthalic acid with paracetamidooanethoil at 210° ; it crystallises in white or yellow needles melting at 160° , and is very soluble in alcohol or acetic acid, but only sparingly in water. It yields a crystalline *nitro-derivative* which melts at 156° .

Paraethoxyphenylphthalimide is prepared by the same methods as its homologue, the corresponding phenetol derivatives being substituted for those of anethoil. It forms lustrous, yellow needles, melts at 204° , and is very soluble in acetic acid. Its *nitro-derivative* melts at 165° , and crystallises in yellow prisms.

On precipitating the potash solutions of the above imides with hydrochloric or sulphuric acid, the corresponding phthalamic acids are obtained; they are reconverted into the imides by heat.

Paramethoxyphenylphthalamic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, forms white or yellow prisms melting at $149\text{--}150^\circ$. *Paraethoxyphenylphthalamic acid* is obtained in yellowish, acicular prisms melting at 204° . Both acids are soluble in alcohol or acetic acid, and insoluble in water.

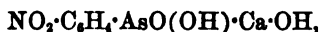
The author attributes the formation of both yellow and white crystals of either imide to the operation of desmotropy.

W. J. P.

Nitrophenylarsen-compounds. By A. MICHAELIS and H. LOESNER (*Ber.*, 27, 263—272).—Phenylarsinic acid, $\text{AsPhO}(\text{OH})_2$, is not acted on by ordinary concentrated nitric acid or by the red fuming acid at 100° . It is, however, easily nitrated by the action of pure nitric acid containing 100 per cent. of HNO_3 , *nitrophenylarsinic acid*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, being formed. This crystallises from water in thin, rhombic plates, and decomposes when heated, water being first given off; it is readily soluble in alcohol, slightly in benzene, insoluble in ether, and is readily soluble in hot water, but only in 200 parts of water at 18° . An anhydride of the acid could not be ob-

tained, since it decomposes before the whole of the water is given off. The relative position of the nitro- and arsenic-groups has not yet been determined. When the acid is heated with bromine and water, orthonitrobromobenzene is formed.

Solutions of the acid give no precipitate with silver nitrate or mercuric chloride; whilst lead acetate and copper sulphate produce insoluble crystalline precipitates. The alkali salts cannot be obtained in a crystalline form. The *barium salt*, $[\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})\cdot\text{O}]_2\text{Ba}$, forms crystalline crusts, whilst the *silver salt*, $\text{C}_6\text{H}_4\text{AsNO}_4\text{Ag}_2$, is a white, amorphous powder. The *calcium salt*,



forms very slender, lustrous plates, and does not lose water when heated. The *copper salt* behaves in a similar manner, and has probably an analogous constitution.

Dinitroarsenobenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{As}\cdot\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, is formed when nitrophenylarsinic acid is boiled with a solution of phosphorous acid. It is a heavy, yellow powder, which is insoluble in the usual solvents. When heated, it decomposes suddenly, and swells up, leaving a voluminous residue of carbon. Oxidising agents convert it into nitrophenylarsinic acid.

Nitrophenylchlorarsine, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsCl}_2$, is obtained by acting on dinitroarsenobenzene suspended in chloroform with chlorine, and treating the unstable *nitrophenyltetrachlorarsine*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsCl}_4$, thus formed with a further quantity of dinitroarsenobenzene. It forms small, white crystals, melts at $46\text{--}47^\circ$, and is not altered by water. *Nitrophenylbromarsine* forms small, white crystals, readily soluble in chloroform, insoluble in light petroleum, and is not altered by water. The corresponding iodine derivative could not be obtained in the crystalline form.

Nitrophenylarsinous acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{As}(\text{OH})_2$, is obtained by the action of alkalis on the foregoing halogen compounds. It forms a white, flocculent precipitate, which is insoluble in water, soluble in alcohol, readily soluble in alkalis, but only with difficulty in alkali carbonates. When heated, it becomes brown, and decomposes without melting.

Nitrophenylarsen disulphide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsS}_2$, is formed when dinitroarsenobenzene is suspended in water and boiled with flowers of sulphur. It is a white powder, melts at about 80° , and decomposes suddenly at a higher temperature. It is readily soluble in aqueous alkalis, slightly in alcohol, insoluble in water and ether.

Nitrophenylarsen sesquisulphide, $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{As})_2\text{S}_3$, is obtained by the action of hydrogen sulphide on an aqueous solution of nitrophenylarsinic acid. It forms small, yellow crystals, melts at 119° , and decomposes suddenly at a higher temperature. It is readily soluble in alkalis, from which acids precipitate it unchanged, but is insoluble in water. Oxidising agents convert it into nitrophenylarsinic acid.

Amidophenylarsen sulphide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsS}$, is formed when an ammoniacal solution of nitrophenylarsinic acid is treated with hydrogen sulphide. It is a white powder which softens at 182° , and melts at 188° to a yellow liquid. It is readily soluble in dilute hydrochloric

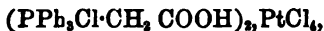
acid, but only slightly in the concentrated acid, the *hydrochloride*, $3\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsS}\cdot 2\text{HCl}$, being sparingly soluble in the strong acid. When boiled with hydrochloric acid, hydrogen sulphide is evolved, *amidophenylarsen chloride*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsCl}_2$, being probably formed; this substance, however, has not been isolated. The sulphate of the amidophenylarsen sulphide, $(\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsS})_2\cdot\text{H}_2\text{SO}_4$, is a white, amorphous powder. A. H.

Betaine and Choline of Triphenylphosphine. By A. MICHAELIS and H. v. GIMBORN (*Ber.*, 27, 272—277).—The *chloride of the ethylic salt of triphenylphosphorbetaine*, $\text{PPh}_3\text{Cl}\cdot\text{CH}_2\cdot\text{COOEt}$, is obtained when ethylic chloracetate is heated with triphenylphosphine. It forms a crystalline powder, which melts at 90° , and is very readily soluble in alcohol, water, &c. The *platinochloride*,



crystallises in small plates. When the ethylic salt is heated at 172° , it decomposes into its constituents. When heated at 90 — 100° , however, it leaves a residue of triphenylmethylphosphonium chloride. The *bromide*, $\text{PPh}_3\text{Br}\cdot\text{CH}_2\cdot\text{COOEt}$, is obtained by mixing concentrated solutions of the chloride and potassium bromide; it melts at 147° . The corresponding *iodide* is obtained in a similar manner, and melts at 165 — 166° .

Triphenylphosphorbetaine, $\text{PPh}_3\langle\text{CH}_2\text{O}\rangle\text{CO}$, cannot be prepared by the action of silver oxide or baryta water on the chloride of the ethylic salt, triphenylphosphine hydroxide, $\text{PPh}_3(\text{OH})_3$, being thus produced. It is, however, formed when concentrated aqueous soda or sodium carbonate is used. It separates from ether in small, tabular crystals, melts at 124 — 126° , and is insoluble in water, readily soluble in alcohol, chloroform, and acetic acid. When heated with water, it is converted into triphenylphosphine hydroxide and acetic acid. It possesses strongly basic properties, and therefore dissolves in dilute acids. The *platinochloride*,



forms long, golden-yellow needles.

Triphenylphosphorcholine hydrochloride, $\text{PPh}_3\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, is prepared by heating ethylene chlorohydrin with triphenylphosphine. It forms white, lustrous needles or transparent tablets, melts at 129 — 130° , and is very readily soluble in water and alcohol, insoluble in ether. The *platinochloride* crystallises in golden-yellow needles, and melts at 222 — 224° .

Triphenylphosphorcholine, obtained by the action of silver oxide on the hydrochloride, is a syrup which slowly crystallises; it has a strong alkaline reaction, and absorbs carbonic anhydride from the air.

Triphenylphosphorcholine hydrobromide forms yellowish-white crystals melting at 114° . The *hydriodide* melts at 185 — 186° .

Trimethylene bromide also combines with the triphenylphosphine,
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forming a compound of the formula $\text{PPh}_3\text{Br}\cdot\text{C}_2\text{H}_5\text{Br}$, which crystallises from alcohol in long, transparent needles, and melts at $226\text{--}228^\circ$. The *platinochloride* is a flocculent precipitate.

A. H.

Aromatic Boron Compounds. By A. MICHAELIS, M. BEHRENS, J. RABINERSON, and W. GEISLER (*Ber.*, **27**, 244—262; compare *Abstr.*, 1880, 395; 1882, 731; 1889, 505).—*Diphenyl borochloride*, BPh_2Cl , is obtained by the action of phenyl borochloride on mercury diphenyl, and separated from the mercuryphenyl chloride simultaneously formed, by boiling with light petroleum, the filtrate being then fractionated. The fraction boiling at $270\text{--}271^\circ$ consists chiefly of diphenyl borochloride, whilst the fraction $271\text{--}272^\circ$ contains some diphenylboric acid. The chloride is a thick, colourless liquid which fumes slightly in the air. It is slowly converted by boiling water into *diphenylboric acid*, $\text{BPh}_2\cdot\text{OH}$, which is a slightly yellow, crystalline mass, melts at $264\text{--}267^\circ$, and has a peculiar penetrating dill-like odour. It gives a beautiful, green flame when ignited in the flame of a bunsen burner.

Orthotolyl borochloride, $\text{C}_6\text{H}_4\text{Me}\cdot\text{BCl}_2$, is obtained by the action of boron chloride on mercury diorthotolyl at $150\text{--}180^\circ$, and forms a thick, colourless liquid which has a pungent odour, solidifies at a low temperature, then melts at 6° , boils at 193° , and is decomposed by water with a hissing noise, with formation of *orthotolylboric acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{B}(\text{OH})_2$. The latter crystallises in slender needles, melts at $160\text{--}161^\circ$, and gives with silver nitrate a yellow precipitate which quickly decomposes into toluene, boric acid, and silver oxide. When dried over sulphuric acid, it loses water, forming *orthotolylboroxide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{BO}$. This melts at the same temperature as the acid, and the latter is probably, therefore, converted into the oxide before it melts.

α -Naphthyl borochloride, $\text{C}_{10}\text{H}_7\cdot\text{BCl}_2$, is obtained by the action of boron chloride on mercury di- α -naphthyl, but, as it does not distil without decomposition, could not be obtained pure. It reacts violently with water, yielding *α -naphthylboric acid*, $\text{C}_{10}\text{H}_7\cdot\text{B}(\text{OH})_2$; the latter crystallises from hot water in slender, colourless needles, becomes plastic at 242° , melts at 259° , and gives with silver nitrate a precipitate, becoming first yellow and finally black, with separation of naphthalene and silver oxide. The acid loses water over sulphuric acid, forming *α -naphthylboron oxide*, $\text{C}_{10}\text{H}_7\cdot\text{BO}$, which is a micro-crystalline powder.

β -Naphthyl borochloride is obtained from boron chloride and mercury β -dinaphthyl. The latter is prepared in the usual manner, by treating β -bromonaphthalene with sodium amalgam in xylene solution containing ethylic acetate, and forms yellowish, nacreous plates or flat needles melting at 238° . It has been converted into the following β -naphthylmercury derivatives; the *chloride*, $\text{C}_{10}\text{H}_7\cdot\text{HgCl}$, crystallising in fascicular aggregates of needles, and melting at 271° ; the *bromide*, $\text{C}_{10}\text{H}_7\cdot\text{HgBr}$, crystallising in flat needles, and melting at 266° ; the *iodide*, $\text{C}_{10}\text{H}_7\cdot\text{HgI}$, forms yellowish plates, melting at 251° ; the *formate*, $\text{C}_{10}\text{H}_7\cdot\text{Hg}\cdot\text{O}\cdot\text{CHO}$, large, colourless, vitreous plates melting at

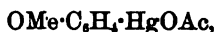
155—158°; and the *acetate*, $C_{10}H_7Hg \cdot OAc$, flat, colourless needles melting at 147—148°.

β-Naphthyl borochloride forms colourless needles, melts at 116°, fumes in the air, and is converted by water into *β-naphthylboric acid*, $C_{10}H_7B(OH)_2$, which exists in two modifications, the first crystallising in broad, colourless plates melting at 248°, and the second in slender needles melting at 266°. The *barium*, *silver*, and *methyllic* salts have been prepared, but are only obtained with difficulty. *β-Naphthylborooxide* crystallises in colourless needles, and melts at 266°.

Attempts to obtain phenylboric acid derivatives containing a hydroxyl group in the phenyl residue were unsuccessful, but the corresponding methoxy- and ethoxy-compounds have been prepared.

Paranisyl borochloride, $OMe \cdot C_6H_4 \cdot BCl_2$, is obtained by acting on mercury diparanisyl with boron chloride at the ordinary temperature; it is a colourless liquid which becomes pale yellow to violet after a time, boils at 182° under 170 mm. pressure, solidifies on cooling, and then melts at 30°. It is violently acted on by water, with formation of *paranisylboric acid*, $OMe \cdot C_6H_4 \cdot B(OH)_2$, which crystallises from water in tabular, probably monosymmetric crystals, and melts at 201—203°. The corresponding oxide could not be obtained.

For the investigation of the orthanisyl compounds, the preparation of *mercury diorthanisyl* was necessary; it was obtained by the usual reaction, and crystallises in monosymmetric prisms melting at 108°. It yields the following mercury orthanisyl derivatives: the *chloride*, $OMe \cdot C_6H_4 \cdot HgCl$, crystallising in small needles or tablets, and melting at 173—174°; the *bromide*, $OMe \cdot C_6H_4 \cdot HgBr$, melting at 183°; the *iodide*, $OMe \cdot C_6H_4 \cdot HgI$, melting at 165°; and the *acetate*,



crystallising in small needles, and melting at 123—124°.

Orthanisyl borochloride, $OMe \cdot C_6H_4 \cdot BCl_2$, was not obtained pure, but yields with water *orthanisylboric acid*, $OMe \cdot C_6H_4 \cdot B(OH)_2$, which crystallises from hot water in small, lustrous plates, and melts at 165°.

The following mercury phenetyl compounds have been prepared in order to obtain the corresponding boron compounds. *Mercury diparaphenetyl*, $Hg(C_6H_4 \cdot OEt)_2$, is formed in the usual manner, crystallises in lustrous, cube-shaped crystals, melts at 135°, and has a sp. gr. of 1.0028 at 15°. It yields the following mercury paraphenetyl compounds: the *chloride*, $OEt \cdot C_6H_4 \cdot HgCl$, melting at 234°; the *bromide*, $OEt \cdot C_6H_4 \cdot HgBr$, melting at 241.5°; the *iodide*, $OEt \cdot C_6H_4 \cdot HgI$, melting at 216°; the *oxide*, $(OEt \cdot C_6H_4 \cdot Hg)_2O$, crystallising in small, white needles, and melting at 202°; the *acetate*, $OEt \cdot C_6H_4 \cdot HgOAc$, crystallising in colourless, rhombohedral tablets or stellate groups of long needles; the *propionate* melting at 116°; the *butyrate* melting at 129°; the *cyanide*, $OEt \cdot C_6H_4 \cdot HgCN$, melting at 158—159°; and the *thiocyanate* melting at 210°. *Mercury diorthophenetyl* crystallises in lustrous needles, and melts at 224°. *Mercury orthophenetyl chloride* forms lustrous needles, melting at 132°; the *bromide*, four-sided prisms, melting at 121°; the *iodide*, thick, prismatic needles, melting at 111°; the *acetate*, white plates melting at 150.5°.

Both mercury diphenetyls are converted by boron chloride at the ordinary temperature into the corresponding borochlorides which yield the analogous boric acids with water. *Paraphenetyl borochloride* is a colourless liquid, which boils at 220° under 400 mm. pressure, readily assumes a reddish colour, and forms a crystalline mass on cooling which melts again at 2° . The corresponding *paraphenetylboric acid*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{B}(\text{OH})_2$, crystallises in lustrous prisms or feathery aggregates of lustrous needles, and melts at 159° . *Orthophenetyl borochloride* has not been obtained pure, but yields with water *orthophenetylboric acid* which crystallises from water in small, white needles, and melts at 171° . Neither of these acids yields an anhydride.

H. G. C.

Isomerism of 1:3-Triketones. By L. CLAISEN (*Ber.*, 27, 114—118).—Tribenzoylmethane, when slowly dissolved in alcoholic sodium ethoxide at 0° , and then precipitated by saturating the solution with carbonic anhydride, is obtained in an isomeric form, which is readily soluble in aqueous sodium carbonate, unlike the original substance, into which it may be reconverted by heating with alcohol. The original substance is probably $\text{CBzO}\cdot\text{CHBz}_2$, the isomeride having the tautomeric constitution $\text{OH}\cdot\text{CBz}\cdot\text{CBz}_2$. The same explanation may be given of the isomerism of the dibenzoylacetones (dibenzoylacetylmethane) (this vol., i, 32). In the series CHBz_2 , CHBz_2Ac , CHBzAc , CHAc_2 , the tendency to form the more acid variety increases, CHAc_2 , being only known in this form, which is the one readily soluble in alkaline carbonates.

C. F. B.

Synthesis of Isocoumarin and of some Derivatives of Isoquinoline. By E. BAMBERGER and W. FREW (*Ber.*, 27, 198—212).—

Isocoumarincarboxylic acid, $\text{C}_6\text{H}_4\cdot\text{CH}(\text{CO}\cdot\text{O})\cdot\text{COOH}$ (*Abstr.*, 1892, 857), does not react with secondary amines, but with primary amines, NH_2R , it yields derivatives $\text{C}_6\text{H}_4\cdot\text{CH}(\text{CO}\cdot\text{NR})\cdot\text{COOH}$. Aniline, ethylamine, and methylamine yield respectively *phenyl-*, *ethyl-*, and *methyl-isocarbostyrlcarboxylic acids*, as yellowish or white prisms, melting at 265° , 202° , and 238° . These substances, when heated, yield respectively *phenyl-*, *ethyl-*, and *methyl-isocarbostyryl*, $\text{C}_6\text{H}_4\cdot\text{CH}(\text{CO}\cdot\text{NR})\cdot\text{CH}$; the first forms white needles, melting at 117.5° ; the others yellowish oils, boiling at 310 — 311° (at 240° under 120 mm.), and 314 — 315° under 720 mm. pressure. The methyl compound eventually solidifies to white plates melting at 40° , and is, doubtless, identical with the substance prepared by Fernau from isoquinoline, and by Decker by oxidising isoquinoline methiodide. Methylisocarbostyryl yields a *dibromide*, which forms a yellowish crystalline powder, melts at 120° , and, when boiled with water, yields *monobromomethylisocarbostyryl* as needles, melting at 132° .

Isocoumarincarboxylic acid may be converted, by the dry distillation of its silver salt, into *isocoumarin*, $\text{C}_6\text{H}_4\cdot\text{CH}(\text{CO}\cdot\text{O})\cdot\text{CH}$, which forms

white crystals, melting at 47°, and boiling at 285—286° under 719 mm. pressure. This substance yields a *dibromide*, crystallising in pyramids, and melting at 135°, and, when heated at 120—130° with alcoholic ammonia, is converted into isocarbostyryl.

When gently warmed with a solution of sodium carbonate, isocoumarin is converted into *anhydro-orthohydroxyvinylbenzoic acid*, $O(\text{CH}:\text{CH}:\text{C}_6\text{H}_4:\text{COOH})_2$. This crystallises in tiny, white needles, melting at 183—184°, and, when heated with dilute hydrochloric acid at 150—160°, yields an *anhydride*, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} & \text{---} & \text{O} & \text{---} & \text{CO} \\ \text{CH}:\text{CH}:\text{O} & \text{---} & \text{CH}:\text{CH} \end{smallmatrix} > \text{C}_6\text{H}_4$, as white needles, melting at 234—235°. The latter substance, when heated with alcoholic ammonia at 170°, yields the corresponding *imide*, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} & \text{---} & \text{NH} & \text{---} & \text{CO} \\ \text{CH}:\text{CH}:\text{O} & \text{---} & \text{CH}:\text{CH} \end{smallmatrix} > \text{C}_6\text{H}_4$, which forms yellow crystals, melting at 285°. The anhydro-acid itself is oxidised by permanganate to phthalic acid; when fused with potash, it yields an acid, $\text{C}_{14}\text{H}_{10}(\text{COOH})_2$, which crystallises in small, white needles and melts at 189°. The constitution of this acid has not yet been determined, but it is certainly not stilbenedicarboxylic acid, as its silver salt yields no stilbene when distilled. C. F. B.

Metaphenylenediacetic acid and the corresponding Nitrile. By G. ODDO (*Gazzetta*, 23, ii, 336—344; compare Kipping, *Trans.*, 1888, 42).—The *potassium* salt of metaphenylenediacetic acid crystallises in transparent prisms containing $7\text{H}_2\text{O}$, of which six are lost in a vacuum over sulphuric acid. The *potassium hydrogen* salt forms anhydrous scales, which melt at 231—232°. The *methylic* salt is a colourless liquid, which boils at 298—300°, and has a pleasant odour. By the action of sulphuric acid on metaphenylenediacetonitrile, a yellowish substance is produced, which contains oxygen, but whose composition could not be determined. W. J. P.

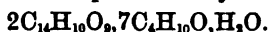
The β -Oxalkylbenzylmalonic acids. By C. LIEBERMANN (*Ber.*, 27, 289—293; compare *Abstr.*, 1893, i, 583).—The methylic and ethylic salts of benzalmalonic acid solidify at winter temperatures in crystals. The *methylic* salt melts at 41° and boils at 210—215° at 60 mm., whilst the *ethylic* salt (*Ann.*, 218, 133) melts at 27—29°.

β -Methoxybenzylmalonic acid, $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}(\text{COOH})_2$, obtained by adding sodium methoxide to methylic benzalmalonate and decomposing this salt with baryta water, is a white crystalline powder, which is moderately soluble in cold water, readily in alcohol, but almost insoluble in benzene. Its ethereal solution does not decolorise bromine, and it is only oxidised by permanganate in solution in sodium carbonate after a little time. When heated, it melts at about 115°, methylic alcohol being given off and benzalmalonic acid formed, which immediately solidifies, and then melts at 197° with evolution of carbonic anhydride. This decomposition into methylic alcohol and benzalmalonic acid is quantitative at 120°. The *barium salt*, $\text{C}_{11}\text{H}_{10}\text{O}_5\cdot\text{Ba} + 2\text{H}_2\text{O}$, is precipitated almost immediately when barium chloride is added to a neutral solution of the acid in ammonia, differing in this respect from that of benzalmalonic acid.

Ethoxybenzylmalonic acid, $\text{OEt} \cdot \text{CHPh} \cdot \text{CH}(\text{COOH})_2$, is a similar substance, and, as well as its ethereal salts, decomposes when heated with elimination of ethylic alcohol. The barium salt has been previously described by Claisen and Crismer. The behaviour of these substances as saturated compounds is used by the author as an argument, against the formula proposed by Nef (*Annalen*, 266, 68) for ethylic sodiomalonate. A. H.

Bismuth Gallanilide. By P. CAZENEUVE (*Bull. Soc. Chim.*, 9, [3], 852—853; compare Abstr., 1893, i, 638).—*Bismuth gallanilide*, $\text{NHPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4(\text{O}_3\text{Bi})_2\text{H}_2\text{O}$, is prepared by adding a boiling aqueous solution of gallanilide (5 grams in 200 c.c.) to a solution of crystallised bismuth nitrate (15 grams) in dilute acetic acid (30 grams acid and 250 c.c. water). It is a yellow powder, which is insoluble in water and the usual solvents, and loses its water of crystallisation at 120° . The existence of this compound tends to confirm the formula $\text{COOH} \cdot \text{C}_6\text{H}_4(\text{O}_3\text{Bi})_2\text{H}_2\text{O}$, assigned by Causse (Abstr., 1893, i, 643) to basic bismuth gallate. JN. W.

Tannin and its Estimation. By P. SISLEY (*Bull. Soc. Chim.*, [3], 9, 755—772).—The least coloured portions of dried and roughly-crushed Chinese gall nuts are extracted with cold water, the colouring matter precipitated with lead acetate, and the nearly colourless extract shaken with ether. The emulsion separates into three layers, the lowest of which consists of a syrupy solution of tannin in moist ether, having a composition represented by the formula



This syrup is dissolved in the minimum quantity of water, repeatedly shaken with ether to remove impurities, and the water and ether removed in a vacuum over sulphuric acid. After recrystallisation from ether, the product is pure *tannin*, a white odourless powder, soluble in all proportions of water to a clear, colourless solution, and yielding a perfectly white lead compound. The gallic acid obtained by hydrolysis of this pure material contains no trace of glucose. (For the method of estimation see this vol., ii, 169).

JN. W.

Action of Sodium Ethoxide on Ethylic Phthalate and Ketones, and on Ethylic Phthalate and Ethylic Succinate. By E. SCHWERIN (*Ber.*, 27, 104—114).—*Acetyl- α -diketohydrindene*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{CHAc}$, is prepared by heating ethylic phthalate, acetone, and sodium ethoxide in alcoholic solution on the water bath, in a reflux apparatus; the resulting sodium salt, which probably has the formula $\text{CHNaAc} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COONa}$, is decomposed by carbonic anhydride, and, after purification, the hydrindene crystallises in yellow needles melting at 110° . The *phenylhydrazone*, $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_3$, is deposited in colourless needles, melts at 184 — 185° , and gives an intense violet coloration with sulphuric acid and ferric chloride. The *barium salt*, $\text{C}_{11}\text{H}_8\text{O}_4\text{Ba} + \text{H}_2\text{O}$, is amorphous. *Benzoyl- α -diketohydrindene*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{CHBz}$, is prepared in a similar manner from ethylic

phthalate and acetophenone, and crystallises in colourless needles, which become yellow on exposure to air, and melt at 108° . The *sodium salt*, $\text{CHNaBz}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COONa}$, and the *barium salt* have also been prepared. The *trioxime* crystallises in colourless needles with $1\text{H}_2\text{O}$, darkens at 207° , and melts at 232° with decomposition. The *triphenylhydrazone* is crystalline; it darkens at about 120° , and melts at $163\text{--}167^{\circ}$. By the action of sodium ethoxide on the hydrindene a *sodium salt* is obtained, which probably has the formula $\text{C}_{16}\text{H}_9\text{O}_3\text{Na} + \text{C}_2\text{H}_5\cdot\text{OH}$; it is decomposed by acids, the hydrindene being regenerated.

Propionyl- α,γ -diketohydrindene, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\rangle\text{CH}\cdot\text{COEt}$, is formed from ethylic phthalate and ethyl methyl ketone, and crystallises in pale yellow needles melting at 103° ; it sublimes on further heating, and readily dissolves in alkalis and alkaline carbonates. The *sodium salt*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\rangle\text{CNa}\cdot\text{COEt}$, is deposited in yellow needles. By the action of ethylic phthalate, ethylic succinate, and sodium ethoxide, in molecular proportion, a compound is obtained which, after purification from ethylic succinosuccinate, crystallises in colourless needles; it reduces alkaline copper solution on warming, gives in alcoholic solution a greenish coloration with ferric chloride, and dissolves in alkalis. From its mode of formation and properties this substance is probably *ethylic hydronaphthaquinonecarboxylate*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO}\cdot\text{CH}\cdot\text{COOEt}\\\text{CO}\cdot\text{CH}\cdot\text{COOEt}\end{smallmatrix}\rangle$. The free acid could not be obtained, but, by the action of sodium ethoxide (2 mols.) on ethylic phthalate (1 mol.) and ethylic succinate (1 mol.), a compound, $\text{C}_{12}\text{H}_9\text{O}_6$, is formed, which crystallises in colourless, rhombic plates, melts at 120° , and is soluble in alkalis; on acidifying, a precipitate is obtained differing from the original substance, but it has not been further investigated. Whether either of these compounds is hydronaphthaquinonecarboxylic acid remains undetermined. J. B. T.

Derivatives of 2'-Phenylindazole. By C. PAAL and C. LÜCKE (Ber., 27, 47—52; compare Abstr., 1891, 723).—2'-Phenylindazole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{N}\\\text{CH}\end{smallmatrix}\rangle\text{NPh}$, is converted by oxidation with chromic acid (Ber., 24, 3058), alkaline permanganate, or dilute nitric acid into azobenzeneorthocarboxylic acid.

α -Nitrophenylindazole, $\text{C}_{12}\text{H}_9\text{N}_2\cdot\text{NO}_2$, is obtained, together with the β -derivative, by the action of fuming nitric acid in the cold on phenylindazole. It crystallises in golden, lustrous plates, melting at 184° . When oxidised with chromic acid, it is converted into *nitro-azobenzeneorthocarboxylic acid*, $\text{NO}_2\cdot\text{C}_{12}\text{H}_9\text{N}_2\cdot\text{COOH}$, which crystallises from dilute alcohol in splendid red needles, melting at 135° .

β -Nitrophenylindazole forms concentric groups of small, light, yellow needles, melting at 174° .

Tribromophenylindazole, $\text{C}_{12}\text{H}_7\text{Br}_3\text{N}_2$, is the chief product obtained by boiling phenylindazole with bromine. It crystallises from acetic

acid in white needles, melting at 204° . This substance is not attacked when boiled with an acetic acid solution of chromic anhydride. *Bromophenylindazole*, $C_{13}H_9BrN_2$, is readily soluble in alcohol and acetic acid, and crystallises in small, almost white needles, melting at 147° . It appears to differ from the derivative synthetically prepared from orthonitrobenzylparabromaniline.

Phenylindazole- α -sulphonic acid, $C_{13}H_9N_2 \cdot SO_3H$, is formed, together with the β -compound, when phenylindazole is heated with fuming sulphuric acid at 120 – 130° . It crystallises in white, radiating needles, which are readily soluble in hot water, almost insoluble in alcohol, and blacken at about 300° . The β -acid is less readily soluble in water, and is formed in smaller quantity; it crystallises in small, white granules, which blacken at about 320° . The *sodium salt* of the α -acid forms white needles, the *barium salt* is moderately soluble in hot water, and forms elongated plates, and the *lead salt* crystallises in white, nacreous plates.

The *barium salt* of the β -acid is only very slightly soluble in water, and forms small granules. A. H.

Reduction of Benzilidioximes. By F. FEIST (*Ber.*, 27, 213–215).—*Diphenylethylenediamine*, $NH_2 \cdot CHPh \cdot CHPh \cdot NH_2$, was obtained, after several unsuccessful attempts, from both α - and β -benzilidioxime, by reducing them with metallic sodium in ethyl-alcoholic solution. It forms white, feathery crystals, and melts at 90 – 92° . The white *hydrochloride*, $C_{14}H_{16}N_2 \cdot 2HCl + 2H_2O$, melts with decomposition at 248° , the yellow *picrate*, $C_{14}H_{16}N_2 \cdot 2C_6H_5N_3O_7$, at 220° ; the yellow *platinochloride*, $C_{14}H_{16}N_2 \cdot H_2PtCl_6 + 2H_2O$, decomposes at 222 – 225° without melting. C. F. B.

Paramidotriphenylmethane. By O. FISCHER and R. ALBERT (*Ber.*, 26, 3079–3082).—Paramidotriphenylmethane may, as already stated (*Abstr.*, 1891, 693), be converted into the corresponding nitrile and carboxylic acid; the former is obtained by Sandmeyer's reaction, and forms vitreous prisms, which melt at 99° ; it distils without decomposition, and, on hydrolysis, yields triphenylmethane-paracarboxylic acid, $CHPh_2 \cdot C_6H_4 \cdot COOH$. The latter, after repeated crystallisation from dilute acetic acid, forms white needles, and melts at 161° . The statement of Oppenheimer (*Abstr.*, 1886, 946) that this acid melts above 350° is, therefore, incorrect. On oxidation with chromic acid in acetic acid solution, triphenylmethaneparacarboxylic acid yields the corresponding *triphenylcarbinolparacarboxylic acid*, $HO \cdot CPh_2 \cdot C_6H_4 \cdot COOH$, which crystallises in fascicular aggregates of white needles, melts at 200° , and is identical with the compound obtained by Hemilian from diphenylmethylphenylmethane (this *Journal*, 1875, 152).

Paramidotriphenylmethane readily undergoes condensation with aldehydes yielding crystalline compounds; the *benzylidene* derivative, $CHPh_2 \cdot C_6H_4 \cdot N \cdot CHPh$, crystallises from alcohol in colourless needles, and melts at 135 – 136° ; the *ortho*hydroxybenzylidene derivative forms yellow, lustrous needles, and melts at 138° ; the *para*nitrobenzylidene

and *orthonitrobenzylidene* derivatives also crystallise in yellow needles, and melt at 126—127° and 114—115° respectively.

When diazotised and treated with an alcoholic solution of β -naphthol, paramidotriphenylmethane yields an azo-colouring matter, *triphenylmethaneazo- β -naphthol*, which crystallises in long, red needles. Resorcinol and α -naphthylamine yield similar colouring matters.

H. G. C.

Constitution of Rosanilines. By A. ROSENSTIEHL (*Bull. Soc. Chim.*, [3], 9, 833—847; compare Abstr., 1893, i, 332).—The author's recent observation of the assumption of a fourth molecule of hydrogen chloride by the di- and tri-amido-derivatives of triphenylmethane and analogous compounds (Abstr., 1893, i, 332) is of importance as tending to disprove the formula, $C_6H_4 < \begin{smallmatrix} C(C_6H_4 \cdot NH_2)_2 \\ NH \end{smallmatrix} HCl$, proposed by Fischer for pararosanine hydrochloride, a formula containing the group, $C_6H_4 < \begin{smallmatrix} C= \\ NH \end{smallmatrix}$, supposed to be common to all coloured substances of this class.

Miolatti's recent work on the conductivity of pararosanine hydrochloride (Abstr., 1893, i, 572) is distinctly in favour of the present author's "ethereal salt" formula, $C(C_6H_4 \cdot NH_2)_3Cl$, and against Fischer's, for the fact that the conductivity does not materially increase with dilution shows that the salt, unlike the di- and tri-hydrochlorides, is not a true electrolyte, and is, therefore, not the salt of an amine. The actual conductivity observed by Miolatti is small, and may very well be due to the action of the basic groups, since it is known from Ostwald's work that many amines are conductors.

Fischer and Jennings' recent criticism (Abstr., 1893, i, 711) of the author's formula, based on certain observations on pararosanine hydrocyanide and hydrochloride may be turned readily against them. The hydrocyanide, admitted by them to be triamidotriphenylacetone nitrile, was contrasted with the hydrochloride with the view of proving that the constitutions of the two substances must be dissimilar. It is true that the former is colourless and insoluble in water, whilst the latter is coloured and soluble; but since colour and solubility are not yet represented in chemical formula, the argument is of little weight. It is also true that the nitrile is stable, and the hydrochloride unstable, towards alkalis; but this is precisely what is to be expected from cyano- and chloro-derivatives of a substituted methane. The complex series of changes, again, which Fischer and Jennings are compelled to assume in the conversion of pararosanine hydrochloride into triamidotriphenylcarbinol, is quite unnecessary if the author's view be taken, the action then appearing as normal, simple hydrolysis. As to rosolic and auric acids, to which Fischer and Jennings assign formulæ analogous to their rosanine formula, it is the metallic salts which are coloured, and not the anhydrides. Sodium aurate and the corresponding hydrochloride may well be represented by the formulæ $C(C_6H_4 \cdot OH)_3 \cdot ONa$ and $C(C_6H_4 \cdot OH)_3Cl$, thus accentuating analogies which Fischer's formulæ pass over. The anhydride

may certainly have the formula assigned to it by Nietzki, but it is not a substance in any way analogous to the others under discussion.

With regard to the contention that the assumption by pararosaniline of a fourth mol. of hydrogen chloride augments the probability of Nietzki's quinonoid formula, it is to be observed that quinone, in taking up hydrogen chloride, loses the characteristic quinonoid structure simultaneously with its colour.

Triamidotriphenylcarbinol and its analogues then form two classes of salts:—Ethereal salts, of which "rosaniline hydrochloride" is a type, and additive or ammonium salts, of which the di-, tri-, and tetra-hydrochlorides are types. JN. W.

Naphthaquinone Chlorimides. By P. FRIEDLÄNDER and O. REINHARDT (*Ber.*, 27, 238—244).—1 : 4-Naphthaquinone chlorimide, $O:C_{10}H_6 \cdot NCl$, is readily obtained by the action of a solution of bleaching powder on 1 : 4-amidonaphthol at 0° . It forms hair-like, yellow needles, and, after recrystallisation from alcohol or acetic acid, melts at 109.5° , and decomposes with a slight explosion at 130 — 133° . It slowly becomes brown at 80° , colours the skin brown, and is reconverted by stannous chloride into 1 : 4-amidonaphthol. With concentrated hydrochloric acid, it yields 2 : 3-dichloro-1 : 4-naphthaquinone, differing in this respect from quinonechlorimide, which yields dichloramidophenol or tetraphenylenediamine. Hydroxylamine converts the chlorimide into 1 : 4-nitrosonaphthol, which the authors find to melt at 193 — 194° .

β -Naphthaquinone- α -chlorimide is obtained in a similar manner to the 1 : 4-derivative, but is much more unstable than this compound. It forms felted aggregates of slender, yellow needles, melts at 86 — 87° , and colours the skin brown. It dissolves in a solution of sodium hydrogen sulphite, yielding 1 : 2 : 4-amidonaphtholsulphonic acid, which crystallises in slender, white needles, and rapidly becomes violet when moist. The α -chlorimide yields α -nitroso- β -naphthol with hydroxylamine.

β -Naphthaquinone- β -chlorimide, prepared from 2 : 1-amidonaphthol forms brownish-yellow needles, decomposes without melting at 98° , and yields with sodium hydrogen sulphite 2 : 1 : 4-amidonaphtholsulphonic acid, and with hydroxylamine, β -nitroso- α -naphthol.

All these naphthaquinone chlorimides yield resinous products with ammonia and phenylhydrazine, and, unlike quinonechlorimide, do not combine with tertiary bases to form colouring matters. Aniline converts them into quinoneanilides.

β -Naphthaquinonedichlorodiimide, $C_{10}H_6(NCl)_2$, is formed by the action of bleaching powder on 1 : 2-naphthylenediamine. It forms yellow needles, is very unstable, melts at 105° , and decomposes at 120° . It is reconverted by stannous chloride into the diamine.

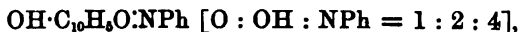
H. G. C.

Action of α - and β -Naphthylamine with Nitrobenzaldehydes. By E. ZENONI (*Gazzetta*, 23, ii, 519).—The condensation products of the nitrobenzaldehydes with the naphthylamines have the constitution $NO_2 \cdot C_6H_4 \cdot CH:N \cdot C_{10}H_7$ in place of that indicated by the author (this vol., i, 137).

/W. J. P.

1:2-Amidonaphthol-4-sulphonic acid. By M. BÖNIGER (*Ber.*, 27, 23—30).—1:2-Amidonaphthol-4-sulphonic acid, which is identical with the compound described by Schmidt (*Abstr.*, 1892, 476), is prepared by dissolving 1:2-nitrosonaphthol in cold sodium hydrogen sulphite solution, heating the liquid to 30—40°, and acidifying with hydrochloric acid. The sulphonic acid separates as a white, crystalline powder, with a faint tinge of red, and is insoluble in boiling water. When its solution in boiling, aqueous sodium hydrogen sulphite is allowed to cool, the *acid sodium salt*, $\text{OH}\cdot\text{C}_{10}\text{H}_7(\text{NH}_2)\cdot\text{SO}_3\text{Na}$, separates in faintly yellow needles, which readily become red in the light. This salt dissolves in boiling water to a small extent, and its solution has a blue fluorescence. As a photographic developer it closely resembles "eikonogen."

1:2-Naphthaquinone-4-sulphonic acid is prepared (German Patent, S. 7608) by treating the amidonaphtholsulphonic acid with $1\frac{1}{2}$ parts of nitric acid of 20 per cent., dissolving in water the ammonium salt which separates, and adding a concentrated solution of potassium chloride. The *potassium salt* is thus formed in golden-yellow needles, which deflagrate at 170—175°. When this salt is treated in aqueous solution with aniline, anilidonaphthaquinone,



is formed; this crystallises from alcohol in needles with a golden lustre, which melt above 240° with decomposition. When boiled with alcohol and sulphuric acid, it is converted into β -hydroxy- α -naphthaquinone, $\text{OH}\cdot\text{C}_{10}\text{H}_6\text{O}_2$, melting at 190°, its constitution and that of the amidonaphtholsulphonic acid being thus proved. Naphthaquinone-sulphonic acid reacts in a similar manner with other primary amines, and also with other compounds containing the amido-group, derivatives of β -hydroxy- α -naphthaquinone being formed. The compound obtained from amidoazobenzene, $\text{OH}\cdot\text{C}_{10}\text{H}_6\text{O}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{Ph}$, is insoluble in water and dilute acids, soluble without change in dilute alkalis, and slightly soluble in alcohol, from which it crystallises in fine red needles melting, with decomposition, at about 250°. The derivative of paraphenylenediamine, $\text{OH}\cdot\text{C}_{10}\text{H}_6\text{O}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, is a bluish-red precipitate which is insoluble in water, readily soluble in dilute alkalis, and slightly soluble in dilute mineral acids; it decomposes above 280° without melting. Sulphanilic acid yields a compound of the formula $\text{OH}\cdot\text{C}_{10}\text{H}_6\text{O}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Na}$, which crystallises in lustrous, yellowish-red plates, and, as well as the free acid, is readily soluble in water and concentrated sulphuric acid. Sodium naphthionate produces a brownish-red substance which has similar properties. Paramidodimethylaniline reacts with the naphthaquinonesulphonic acid to form a compound of the formula $\text{OH}\cdot\text{C}_{10}\text{H}_6\text{O}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, which is a derivative of β -hydroxyindophenol. It dissolves readily in dilute alkalis or acids, is insoluble in water, but soluble in alcohol, and melts and froths up at 232°. Like indophenol, it may be reduced by tin acetate to the leuco-compound $\text{C}_{10}\text{H}_8(\text{OH})_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, which is readily soluble in acetic acid, and may be applied in calico printing, but gives colours which are destroyed by alkalis. Paramidoethylbenzylaniline-sulphonic acid yields a similar derivative.

When heated with aniline and aniline hydrochloride at 120° , 1 : 2-naphthaquinonesulphonic acid is converted into anilidonaphthaquinoneanil, melting at 180° , $\text{NHPh}\cdot\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{NPh}$, and it can therefore be converted into rosindulines. The indulines prepared from potassium naphthaquinonesulphonate and the products of its reaction with paraphenylenediamine and dimethylparaphenylenediamine are readily soluble, and closely resemble the colouring matters known as paraphenylene violet, &c., obtained from paraphenylenediamine and amidoazobenzene.

1 : 2-Naphthaquinol-4-sulphonic acid is formed when the naphthaquinone compound is reduced with sulphurous acid, and has been previously obtained by the action of sodium hydrogen sulphite on β -naphthaquinone.

2 : 1-Nitrosonaphthol, when treated with bisulphite, yields the corresponding 2 : 1-amidonaphthol-4-sulphonic acid, which is also converted by oxidation into 1 : 2-naphthaquinone-4-sulphonic acid. A. H.

Syntheses in the Acridine Series ; 2 : 2'-Phenylamidonaphthol. By O. FISCHER and H. SCHÜTTE (*Ber.*, **26**, 3085—3089).—Nitrodiphenylmethane is slowly converted by tin and boiling hydrochloric acid into amidodiphenylmethane, $\text{CH}_3\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, the hydrochloride of which is isolated in the usual manner, and forms colourless, nodular, crystalline aggregates melting at 175° ; the free base is an oil which volatilises in a current of steam. The acetyl derivative crystallises in stellate groups of needles, and melts at 135° . When passed through a layer of lead oxide 15 cm. in length, heated to moderate redness, amidodiphenylmethane is converted into acridine.

When β -dinaphthylmetaphenylenediamine is fused with benzoic acid and zinc chloride, it is converted into β -naphthalidomesophenylphenonaphthacridine, $\text{C}_{10}\text{H}_7\cdot\text{N}(\text{C}_6\text{H}_5)_2\cdot\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, which crystallises from benzene in yellow needles melting at 244° , and gives solutions having a yellowish-green fluorescence. The salts form red colouring matters, but show no distinct fluorescence. The β -dinaphthylmetaphenylenediamine was prepared by heating β -naphthylamine and metaphenylenediamine together at 300° for some time, and melts at 192° ; the compound described by Ruhemann (*Abstr.*, 1882, 391) under this name is in reality the mononaphthyl derivative (compare *Abstr.*, 1893, i, 420).

2 : 2'-Phenylamidonaphthol, obtained by Hepp from 2 : 2'-dihydroxynaphthalene, crystallises in small white needles, and melts at 160° . In alcoholic solution, ferric chloride gives with it a dark, flocculent precipitate, and bromine a red precipitate; it readily reduces solutions of silver salts, and has no pronounced basic properties. The hydrogen of the hydroxyl group may be readily displaced by alkyl or acyl groups; the acetyl derivative forms stellate groups of white needles, and melts at 162° , the benzoyl derivative colourless lustrous needles melting at 137° , the methyl ether white, silky needles melting at 137 — 138° , and the ethyl ether stellate groups of white needles melting at 164° . Both the last-named compounds are insoluble in dilute alkalis, and show a reddish-blue fluorescence in alcoholic solution.

When heated with formic acid and zinc chloride, or benzoic chloride and zinc chloride, phenylamidonaphthol also yields acridine derivatives, but these have not as yet been obtained pure. H. G. C.

Phenolphthaleïn-anilide and Orcinolphthaleïn-anilide. By R. ALBERT (*Ber.*, 26, 3077—3079).—Phenolphthaleïn, like fluoresceïn (Abstr., 1893, i, 721), is acted on by heating with a mixture of aniline and aniline hydrochloride, with formation of *phenolphthaleïn-anilide*, $\text{CO} < \text{C}_6\text{H}_4 > \text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2$, which, after repeated recrystallisation from dilute alcohol, melts at 279°. It imparts to concentrated sulphuric acid a reddish colour, dissolves in alkalis, forming a colourless solution, and is only resolved into phenolphthaleïn and aniline with great difficulty. Its *dimethyl ether* is crystalline, and melts at 192°.

Orcinolphthaleïn-anilide, $\text{CO} < \text{C}_6\text{H}_4 > \text{C} < \text{C}_6\text{H}_4\text{Me}(\text{OH}) > \text{O}$, is obtained in a similar manner to the foregoing compound, and crystallises from alcohol in slender white needles which melt above 300°. It forms colourless solutions in alkalis, but dissolves in concentrated sulphuric acid with a yellowish-red colour. The *dimethylic ether* also forms slender colourless needles, and remains unaltered at 300°.

H. G. C.

Camphene in Essential Oils. By J. BERTRAM and H. WALBAUM (*J. pr. Chem.*, [2], 49, 15—19).—The authors have sought for camphene in oil of lemon, ginger oil, kerso oil (Abstr., 1891, 238), and camphor oil, by taking advantage of the ease with which it may be converted into isoborneol (this vol., i, 204). They have obtained isoborneol from the first three of these, but have not yet come to a decision with regard to camphor oil.

A. G. B.

New Camphor Derivatives. By G. ODDO (*Gazzetta*, 23, ii, 314—335; compare Brühl, Abstr., 1892, 200).—*Dicamphoquinone*, $(\text{C}_{16}\text{H}_{14}\text{O})_2$, is produced on reducing monobromocamphor with sodium in toluene solution at 90°, and then passing a rapid current of carbonic anhydride through the heated solution; the liquid part of the product is then decanted into water, and the toluene solution distilled in a current of steam. The dicamphoquinone comes over after the toluene and camphor have distilled; it forms lustrous, yellow, rectangular plates which melt at 129—130°, after having been heated with acetic anhydride in a sealed tube at 150°, and subsequently recrystallised from dilute alcohol. If the substance is distilled, however, or heated with acetic anhydride at 220—230°, it melts at 148—150° after recrystallisation. It has a pleasant odour, is optically inactive in solution, and is very soluble in alcohol, ether, benzene, chloroform, carbon bisulphide, or acetic acid, but only sparingly so in light petroleum. Dicamphoquinone is found to have the double molecular formula in freezing acetic acid; but although it distils without alteration at 320°, its vapour density could not be determined in a bath of sulphur vapour, owing to decomposition. A small quantity of a substance which melts at 220—222° is formed during the reduction of the bromocamphor; this is still under examination. *Dicamphoquinone*—

hydrazone, $C_{22}H_{40}N_4$, crystallises in white needles melting at $190-191^\circ$, with decomposition, and is soluble in the ordinary solvents. The corresponding oxime could not be prepared. Dicumphoquinone is readily acted on by bromine in acetic acid solution without evolution of hydrogen bromide; 4 atoms of bromine seem to be taken up, but the product is unstable, and could not be purified.

Dicumphoryl, $(C_{10}H_{14}O)_2$, is obtained on reducing dicumphoquinone with zinc dust and sulphuric acid in alcoholic solution; it forms beautiful, colourless needles or scales melting at $160-162^\circ$, and is almost odourless. Cryoscopic determinations in acetic acid solution show that it has the molecular composition given above. It does not react with phenylhydrazine or hydroxylamine, and is soluble in the ordinary organic solvents. A small proportion of *dibornyl*, $(C_{10}H_{14}O)_2$, is also formed in the above method of preparation, and is the principal product if the quinone is reduced by sodium in alcoholic solution. It crystallises in beautiful, pearly scales melting at $164-166^\circ$, reacts with acid chlorides, and is insoluble in all the ordinary organic solvents. The author concludes with a discussion of the foregoing results, and assigns possible constitutional formulæ to the new compounds prepared.

W. J. P.

Derivatives of Cyano-camphor and of Ethereal Salts of Camphocarboxylic acid. By J. MINGUIN (*Ann. Chim. Phys.*, [6], 30, 512-547).—Nearly all the results recorded in this paper have already appeared.

β -Naphthyl cyanocampholate, $CN \cdot CH_2 \cdot C_6H_4 \cdot COOC_{10}H_7$, is obtained by heating cyanocamphor with sodium and *β -naphthol* at 200° in a sealed tube; it forms small, transparent crystals, melts at 117° , and its specific rotatory power in toluene is $[\alpha]_D = +17.1$. When either *β -naphthyl*, *benzyl*, or *phenyl cyanocampholate* (compare also Abstr., 1891, 463, 464) is treated with potash, *hydroxycamphocarboxylic acid* is obtained, whilst from the mother liquor *cyano-campholic acid*, $CN \cdot CH_2 \cdot C_6H_4 \cdot COOH$, melting at 164° (*loc. cit.*), may be separated. The *sodium salt* has a specific rotatory power in alcoholic solution, $[\alpha]_D = +52.47$, whilst the rotatory power of the *barium salt* in aqueous solution is $[\alpha]_D = +67.4$.

Hydroxycamphocarbamie acid, $NH_2 \cdot CO \cdot CH_2 \cdot C_6H_4 \cdot COOH$, is obtained by boiling an alcoholic solution of cyanocamphor or of cyanocampholic acid with potash; it melts at $205-210^\circ$, and its specific rotation in alcoholic solution is $[\alpha]_D = +63.5^\circ$.

When the *azo-derivatives* of cyanocamphor (Abstr., 1892, 1343) are boiled with alcoholic potash, *benzeneazohydroxycamphocarbamie acid*, $COOH \cdot C_6H_4 \cdot CH(N, Ph) \cdot CO \cdot NH_2$, is formed.

A. R. L.

Campholylic Alcohol. By G. ERRERA (*Gazzetta*, 23, ii, 497-500; compare Abstr., 1893, i, 108).—The speed of etherification of campholylic alcohol, when heated with acetic acid at $153-155^\circ$, shows it to be a tertiary alcohol; during the heating, an unsaturated hydrocarbon, probably camphelene, is produced.

W. J. P.

Campholylamine and Camphelic Alcohol. By G. ERRERA (*Gazzetta*, 23, ii, 500—519; compare Abstr., 1892, 1345; 1893, i, 108).—A good yield of campholylamine is obtained by distilling dicamphelylcarbamide with potash; it melts at about 43° and boils at 175·5°. The hydrochloride crystallises in the monosymmetric system, $a : b : c = 2·4929 : 1 : 1·8758$. $\beta = 63^\circ 55'$. The *acetyl* derivative, $C_9H_{17} \cdot NHAc$, is obtained as a fibrous, crystalline mass, whilst the *benzoyl* derivative forms lustrous, colourless laminæ, melting at 96—97°.

Allylcamphelylthiocarbamide, $C_9H_{17} \cdot NH \cdot CS \cdot NH \cdot C_3H_7$, separates on boiling campholylamine with allylthiocarbimide; it crystallises in thin, silky needles melting at 79—80°, and is soluble in alcohol, benzene, or light petroleum.

Phenylcamphelylthiocarbamide, obtained in a manner similar to the preceding, crystallises in lustrous, colourless laminæ, melting at 105—106°.

Camphelylammonium camphelyldithiocarbamate,



is obtained by the action of carbon bisulphide on campholylamine; heat is developed, and the salt separates in large, tabular crystals, which have an unpleasant odour and melt at 95—96°. On heating at 100° hydrogen sulphide is evolved, and *camphelic thiocyanate*, $C_9H_{17}N \cdot CS$, remains, together with campholylamine; the new salt is crystalline and melts at 24°. It has a pleasant odour, and decomposes on distillation, but is volatile in a current of steam. On heating at 100° with campholylamine, it yields dicamphelylthiocarbamide, $CS(NH \cdot C_9H_{17})_2$; it crystallises in colourless prisms melting at 108—109°, and is soluble in the ordinary solvents.

Campholylamine nitrite is obtained in colourless needles by the action of nitrous acid on the base; on heating, it breaks up, giving a mixture of *camphelene*, C_9H_{18} , and *camphelic alcohol*, $C_9H_{17} \cdot OH$. Camphelene is a colourless, mobile oil of pleasant odour, and boils at 132°; it is probably identical with the hydrocarbon obtained in the preparation of campholic chloride (Abstr., 1892, 1345). Camphelic alcohol slowly solidifies to a mass of prismatic crystals melting at 25—26°, and boils at 179—180°; it has a camphor-like odour, volatilises more readily than camphor at ordinary temperatures, and is sparingly soluble in water. Attempts to determine whether it is a primary alcohol or not, from its speed of etherification with acetic acid, were rendered futile by the readiness with which dehydration occurred and camphelene was formed. The alcohol yields a *hydrate*, $C_9H_{17} \cdot OH, \frac{1}{2}H_2O$, when shaken with water; this forms hard, prismatic crystals, melting at 36—37°. On treating the alcohol with hydrogen chloride, a mixture of *camphelic chloride*, $C_9H_{17}Cl$, and camphelene is obtained, which cannot be completely separated by distillation.

Phenylcamphelylsemicarbazide, $NHPh \cdot NH \cdot CO \cdot NH \cdot C_9H_{17}$, is prepared by mixing camphelic isocyanate and phenylhydrazine; it melts at 67—69°.

Diacetonecamphelylcarbamide, $C_9H_{17} \cdot NH \cdot CO \cdot NH \cdot CMe_2 \cdot CH_2Ac$, prepared from camphelic isocyanate and diacetoneamine, crystallises in

lustrous, colourless needles, melting at 115° ; it is sparingly soluble in boiling water, and yields dicamphelylcarbamide on heating above its melting point. W. J. P.

Isoborneol. By J. BERTEAM and H. WALBAUM (*J. pr. Chem.*, [2], 49, 1—15).—*Isoborneol*, $C_{10}H_{18}O$, is obtained by warming camphene with a mixture of acetic acid and a little sulphuric acid and decomposing the resulting acetate by alcoholic potash. It crystallises in laminae, melts in a sealed tube at 212° , sublimes very easily, and dissolves in most organic solvents, but not in water. It is distinguished from borneol (obtained in the usual way from camphor and purified by conversion into its acetate) by its greater volatility, its higher melting point (borneol melts at 203 — 204° and boils at 212°), and its greater solubility in benzene and in light petroleum. At 0° , 1 part of borneol dissolves in 6.5—7 parts of benzene, and 1 part of isoborneol in 2.5—3 parts; at 20° , the solubilities become 1 in 4—4.5, and 1 in 1.5—2 respectively. At 0° , 1 part of borneol dissolves in 10—11 parts of light petroleum, and 1 part of isoborneol in 4—4.5; at 20° , the solubilities become 1 in 6, and 1 in 2.5 respectively.

The crystallography of borneol and isoborneol is given.

Isobornylphenylurethane, $C_{10}H_{17}O \cdot CO \cdot NHPh$, resembles bornylphenylurethane (m. p. 138 — 139° ; Leuckart, Abstr., 1887, 376, gives 133°) in all its properties, save that, when heated with alcoholic potash, isoborneol is among the products.

The bromal derivative of isoborneol melts at 71 — 72° ; the corresponding derivative of borneol melts at 98 — 99° . The chloral derivative of isoborneol does not crystallise; that of borneol melts at 55 — 56° (compare Abstr., 1891, 575; 1893, i, 526).

Isobornylic formate is a colourless liquid, boils at 100° (14 mm.), and is apparently identical with bornylic formate; its specific gravity is 1.017 at 15° .

Isobornylic acetate is a colourless liquid, and boils at 107° (13 mm.); its sp. gr. is 0.9905 at 15° . Bornylic acetate is crystalline, and melts at 29° , but is otherwise similar to the isobornylic salt.

Dehydrating agents convert isoborneol into camphene (m. p. 50° ; b. p. 159 — 160°); borneol is not affected by them. With sulphuric acid and methylic and ethylic alcohols respectively, isobornylic, methylic, and ethylic ethers are obtained respectively. Borneol does not yield ethers by this treatment, but the methylic and ethylic ethers derived from it by other means do not differ in properties from those derived from isoborneol (Abstr., 1892, 200), nor is there any difference in melting point and boiling point between the methylene ethers, camphors, and camphoroximes derived from each.

The borneol of commerce is a mixture of borneol and isoborneol, and in one case consisted of 80 per cent. of the former with 20 per cent. of the latter. A. G. B.

Santonin acid and its Derivatives. By L. FRANCESCONI (*Gazzetta*, 23, ii, 457—468).—On oxidising santonin acid with alkaline permanganate, the author (Abstr., 1892, 1352) obtained a tetracarboxylic acid (α -acid), melting at 176° ; this can be converted

into an isomeric acid (β -acid), which loses 1 mol. H_2O at $135\text{--}145^\circ$, yielding an anhydride. The α -acid has the specific rotation $[\alpha]_D = +28.56^\circ$, whilst, for the β -acid, $[\alpha]_D = 29.16^\circ$.

The *tetramethylic* salt of the α -acid, $\text{C}_{13}\text{H}_{14}\text{O}_6\text{Me}_4$, is a viscous substance, which could not be obtained crystalline; its specific rotatory power $[\alpha]_D = +56.02^\circ$. The *tetramethylic* salt of the β -acid, however, crystallises from ether in lustrous cubes melting at $99\text{--}100^\circ$, and is optically inactive. Since the α -acid can be converted into the β -isomeride, whilst the reverse change cannot be brought about, the isomerism resembles that of the substituted succinic acids and of the hydrophthalic acids.

On heating acetic acid solutions of the α -acid with iodine at $200\text{--}210^\circ$, a *dicarboxylic acid*, $\text{C}_{13}\text{H}_{14}\text{O}_6$, is obtained; it separates from its solutions in colourless crystals melting at $250\text{--}251^\circ$ with decomposition, and is soluble in alcohol, ether, or boiling water. In a 3 per cent. alcoholic solution, its specific rotation $[\alpha]_D = +42.8^\circ$. The *barium* salt crystallises in long, silky needles, containing 1 mol. H_2O , which is lost at 180° . The acid is not acted on by acetic anhydride, and yields two viscid *methylic* salts, which are insoluble in sodium carbonate.

The α -acid decomposes on heating at $280\text{--}300^\circ$ with caustic soda, hydrogen being evolved, and sodium carbonate, sodium acetate, and a *tricarboxylic acid*, $\text{C}_{10}\text{H}_{10}\text{O}_6$, being formed. The new acid crystallises in colourless, microscopic needles, melting at $125\text{--}126^\circ$, and is soluble in water, alcohol, or ether but only sparingly so in benzene, light petroleum, or chloroform. It is optically inactive, and yields a viscid *methylic* salt, which is also inactive and is insoluble in cold alkalis. The *barium* salt, $(\text{C}_{10}\text{H}_{10}\text{O}_6)_2\text{Ba} \cdot 2\text{H}_2\text{O}$, loses $1\text{H}_2\text{O}$ at $140\text{--}160^\circ$; the *silver* salt is obtained as a white precipitate, and is stable towards light.

If the α -acid is heated with caustic soda at 400° , a neutral substance, $\text{C}_6\text{H}_{14}\text{O}$, distils; this is an optically inactive, colourless oil, boiling at $169\text{--}171^\circ$, and has the normal vapour density at 205° . An oily, aliphatic acid, $\text{C}_6\text{H}_{14}\text{O}_6$, or $\text{C}_7\text{H}_{14}\text{O}_6$, is also obtained by heating the α -acid with soda; it boils at above 200° , and has an odour recalling that of isobutyric acid.

On treating the α -acid with red phosphorus and iodine, a *hydrocarbon*, C_8H_{16} , is obtained; it has a pleasant odour, boils at 134° , and is but slowly acted on by bromine, with evolution of hydrogen bromide.

W. J. P.

New Isomerides of Santonin and Santonous acid. By A. ANDREOCCHI (*Gazzetta*, 23, ii, 468—493; compare Abstr., 1893, i, 526).—*Desmotroposantoninic acid*, $\text{C}_{18}\text{H}_{20}\text{O}_4$, is prepared by dissolving desmotroposantonin or its lactone in barium hydroxide, and extracting with ether after acidification; it can be obtained crystalline but soon changes into the lactone. The *barium* salt was prepared.

Methylic desmotroposantonite, $\text{OH} \cdot \text{C}_{14}\text{H}_{18} \cdot \text{COOMe}$, is prepared in the usual way and crystallises in needles or plates melting at $95\text{--}96^\circ$. On heating it in a reflux apparatus with methylic alcohol, methylic iodide, and sodium, under two atmospheres pressure, *methylic methyl-*

desmotroposantonite, $\text{OMe}\cdot\text{C}_{14}\text{H}_{18}\cdot\text{COOMe}$, is obtained. It is a colourless, viscous liquid, which solidifies to a vitreous mass in a freezing mixture, and boils at $300\text{--}305^\circ$ under 80 mm. pressure. *Methyl-desmotroposantonous acid*, $\text{OMe}\cdot\text{C}_{14}\text{H}_{18}\cdot\text{COOH}$, is prepared by dissolving its methylic salt in methylic alcohol, adding soda, saturating with carbonic anhydride, and precipitating with sulphuric acid. It crystallises in small, white prisms melting at $97\text{--}98^\circ$, and is soluble in ether, alcohol, or light petroleum. *Ethylic desmotroposantonite* is obtained as a viscid oil.

On fusing desmotroposantonous acid with potash, it decomposes quantitatively into hydrogen, propionic acid, and 1 : 2 : 4-dimethyl- β -naphthol.

Isodesmotroposantonin, $\text{C}_{15}\text{H}_{18}\text{O}_3$, an isomeride of desmotroposantonin, is obtained by fusing the latter with potash at $210\text{--}220^\circ$; it separates on treating the aqueous solution of the fused product with acid, and crystallises in needles melting at $187\text{--}188^\circ$ with slight decomposition. It is soluble in alcohol or acetic acid, but only sparingly so in ether or hot water, and has the specific rotatory power $[\alpha]_D = +127^\circ 55'$ in a 1.3 per cent. alcoholic solution. The *acetyl* derivative, $\text{C}_{15}\text{H}_{17}\text{AcO}_3$, is obtained in small, transparent prisms melting at 154° , and has the specific rotation $[\alpha]_D = +122^\circ 36'$ in a 1.3 per cent. alcoholic solution.

Isodesmotroposantoninic acid, $\text{OH}\cdot\text{C}_{14}\text{H}_{18}\text{O}\cdot\text{COOH}$, is obtained by dissolving isodesmotroposantonin in barium hydroxide. It crystallises in microscopic, white needles, and soon changes into the lactone. The *barium* salt is crystalline and very soluble in water.

Lævosantonous acid is obtained by reducing isodesmotroposantonin with zinc dust and acetic acid; it crystallises in needles melting at $176\text{--}177^\circ$, and has the specific rotation $[\alpha]_D = -74^\circ 30'$. On crystallising together equal weights of santonous and lævosantonous acids the inactive isosantonous acid prepared by Cannizzarro and Carnelutti is obtained; the latter acid, which melts at $153\text{--}158^\circ$, is therefore the racemic form of the two former ones. *Ethylic lævosantonite* has the specific rotation $[\alpha]_D = -70^\circ 37'$; like ethylic isosantonite, it melts at $116\text{--}117^\circ$. The racemic modification, which was prepared by Cannizzarro (*Gazzetta*, 12, 401), is completely dissociated in freezing acetic acid. The *methylic* salt of the new acid melts at 82° , whilst *methylic isosantonite* melts at $81\text{--}84^\circ$.

The author is continuing the investigation of these substances.

W. J. P.

Chionanthin. By W. v. SCHULZ (*Chem. Centr.*, 1893, ii, 820—821, and 866—867; from *Pharm. Zeit. Russ.*, 32, 579—581 and 593—595).—This glucoside, $\text{C}_{22}\text{H}_{30}\text{O}_{10} + 2\text{H}_2\text{O}$, was isolated from the root-bark of the Virginian snowflake shrub (*Chionanthus virginica*). It crystallises in silky, white spangles, which lose their water of crystallisation at 110° , and, at a higher temperature, turn reddish-violet, and melt to a transparent, glassy mass. Dilute acids hydrolyse it to dextrose and a reddish-brown resinous substance, which melts below 110° . It does not seem very poisonous, and its properties generally differ from those of saponin.

C. F. B.

Chrysin. By G. DARIER (*Ber.*, 27, 21—22).—The author has confirmed the results obtained by Kostanecki (this vol., i, 93) in the examination of the acetyl compound of tectochrysin, and has also studied the action of nitric acid on chrysin. *Dinitrochrysin*, $C_{15}H_8O_4(NO_2)_2$, is obtained by boiling chrysin with nitric acid of sp. gr. 1.35. It crystallises from alcohol in rose-red plates, which are only very slightly soluble in water, rather more freely in alcohol, and melt at 272° (uncorr.). When treated with acetic anhydride it is converted into *diacetyldinitrochrysin*, $C_{15}H_6O_4(NO_2)_2(OAc)_2$, which crystallises from benzene in yellow needles and melts at 229° (uncorr.). The dinitro-compound forms a yellow crystalline *potassium salt*, $C_{15}H_6O_4(NO_2)_2(OK)_2 + H_2O$, and a *calcium salt*, of the formula $C_{15}H_6O_4(NO_2)_2(O_2Ca)$. The composition of these substances may be regarded as a further proof of the existence of two hydroxyl groups in chrysin. A. H.

Action of Benzaldehyde on Symmetrical Trimethylpyridine.
By H. DUBKE (*Ber.*, 27, 79—86).—2 : 4-Dimethyl- α -stilbazole,
 $C_5NH_3Me_2 \cdot CH : CHPh$,

is prepared by heating trimethylpyridine with benzaldehyde and zinc chloride for six hours at 137 — 140° ; after purification it is separated from 2 : 4-dimethylpyridylmethylenephénylalkine (see below) by means of mercuric chloride, and forms a yellowish-brown syrup which boils, with slight decomposition, at 188 — 189° under a pressure of 9 mm. The *hydrochloride* crystallises in prisms with $2H_2O$, softens at 208° , and melts at 215 — 217° . The *hydrobromide*, with $2H_2O$, forms slender, yellow needles melting at 218 — 220° . The *nitrate* crystallises in slender, colourless needles with $2H_2O$, and melts at 95 — 105° . The *mercurochloride*, $C_{15}H_{11}N, HgHCl_2 + H_2O$, is almost insoluble in water; it forms slender, yellow needles, softens at 208° , and melts at 218 — 219° with decomposition. The *aurochloride* crystallises in anhydrous needles and melts at 189 — 191° . The *platinochloride* forms yellowish-red needles, which melt at 230 — 232° with previous blackening at 220° . The *picrate* is crystalline, blackens at 230° , and melts at 240 — 241° with decomposition. On treatment of the base with bromine in carbon bisulphide solution, hydrogen bromide is evolved, and three compounds containing bromine are formed; they are crystalline, and melt at 213 — 214° , 167 — 168° , and 200° respectively. On reduction with sodium in alcoholic solution, the 2 : 4-dimethyl- α -stilbazole yields 2 : 4-dimethyl- α -stilbazoline, $C_5NH_3Me_2 \cdot CH_2 \cdot CH_2Ph$, in small quantity; it is an oily liquid and forms a crystalline *hydrochloride*, which melts at 160° — 162° with decomposition. 2 : 4-dimethylpyridylmethylenephénylalkine, $C_5H_7NMe_2 \cdot CH_2 \cdot CHPh \cdot OH$ (see above), is a greenish-yellow, fluorescent, oily liquid, boiling, with partial decomposition, between 50° and 148° under 9 mm. pressure. The *hydrochloride* crystallises with $\frac{1}{2}$ mol. H_2O , and melts at 209 — 211° . The *hydrobromide* is deposited in slender, colourless, anhydrous crystals, melting at 187 — 188° . The *mercurochloride* and *aurochloride* each crystallise with $1H_2O$ and melt at 99 — 101° and 138 — 140° respectively. The *platinochloride*, $(C_{15}H_{11}NO)_3, H_2PtCl_6 + 2H_2O$, forms yellowish-red crystals, which melt at 125 — 130° with previous soften-

ing at 105°. The *picrate* crystallises in slender needles and melts at 124—125°. J. B. T.

Action of Chloral on Aldehydecollidine. By P. SCHUBERT (*Ber.*, 27, 86—90).— β -Ethylpyridyl- α -trichlorohydroxypropane,

$$C_5NH_5Et\cdot CH_2\cdot CH(OH)\cdot CCl_3,$$

is prepared by heating collidine with chloral in presence of amylic acetate for six hours at 140—150°; it is purified by means of the hydrochloride, and crystallises from alcohol, on the addition of water, in colourless plates melting at 86°. The *hydrochloride*, $C_{10}H_{13}Cl_3O\cdot HCl$, forms transparent prisms, melting at 175—176° with decomposition. The *hydrobromide* is deposited in yellow prisms which darken at 185° and melt at 188°. The *hydriodide* is unstable, forms prismatic plates, and melts at 174°. The *platinochloride* crystallises in pale yellow plates melting at 208°. The *picrate* is deposited in yellow needles and melts at 150°. The *dichromate* crystallises in bronze plates and explodes violently at 118°. The *aurochloride* and *mercurochloride* are oily.

By the action of potassium carbonate on the base, α -ethylpyridyl- β -lactic acid, $C_5NH_5Et\cdot CH_2\cdot CH(OH)\cdot COOH$, is formed, and crystallises from a mixture of chloroform and light petroleum in small, lustrous plates melting at 66°. The *hydrochloride* is syrupy; the *aurochloride* crystallises with $1H_2O$, and melts at 83—84°. The *calcium salt*, $(C_{10}H_{13}NO_3)_2Ca + \frac{1}{2}H_2O$, is deposited in plates melting at 105° with previous softening at 100°. The *strontium salt* is anhydrous and crystalline, and melts at 143—144°. The *barium*, *zinc*, and *copper salts* have also been prepared; the first two are gelatinous, the last sparingly soluble.

On heating ethylpyridyltrichlorohydroxypropane with alcoholic potash, the water is eliminated and *ethylpyridylacrylic acid*, $C_5NH_5Et\cdot CH:CH\cdot COOH$, is formed; it crystallises from water in stellate needles, melts at 137°, and readily dissolves in sodium carbonate. The *hydrochloride* is deposited in broad plates melting at 195—197° with decomposition and previous blackening at 170°. The *aurochloride* forms prisms melting at 98°. The *mercurochloride* crystallises in pale yellow plates and melts at 142°.

J. B. T.

Resolution of β -Pipecoline and Tetrahydroquinaldine into their Optical Isomerides. By A. LADENBURG (*Ber.*, 27, 75—78).— β -Pipecoline is converted into the *hydrogen tartarate* and the salt recrystallised seven times at ordinary temperatures; it forms hemimorphous monoclinic crystals, $a : b : c = 1.27403 : 1 : 0.73645$; $\beta = 98^\circ 18'$, and melts at 170—172°. The active base boils at 124°, and the refractive power $[\alpha]_D = -3.98^\circ$ at 25°. These figures are approximate only, as the base was obtained in very small quantity. Tetrahydroquinaldine boils at 250° (corr.), its sp. gr. = 1.042 at 16°/4°. The *hydrogen tartarate* forms hemimorphous, monoclinic crystals, $a : b : c = 1.37956 : 1 : 1.05254$; $\beta = 118^\circ 38'$. The refractive power of the free base $[\alpha]_D = 55^\circ 99'$ at 16°.

J. B. T.

Methyltetrahydroisoquinoline Methiodide. By A. FERRATINI (*Gazzetta*, 23, ii, 409—415).—The oily base which the author has

previously obtained (Abstr., 1893, i, 227) by distilling methyltetrahydroisoquinoline with potash is most probably *orthovinyltrimethylbenzylamine*, $\text{CH}_2\text{:CH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_3$. On treating its carbon bisulphide solution with bromine, it yields a crystalline *hydrobromide*, $\text{C}_{11}\text{H}_{14}\text{NBr}\cdot\text{HBr}$, which melts at 108° ; a small quantity of a second white, crystalline *substance*, which melts at 186° , is also obtained. The methiodide gives off trimethylamine and carbonises on heating, thus behaving in the same way as Freund's methylhydrohydrastine methiodide (Abstr., 1893, i, 116) which it resembles in constitution. Trimethylamine is also evolved on distilling the methiodide with potash. On shaking the methiodide in aqueous solution with freshly precipitated silver chloride, a crystalline *hydrochloride* is obtained which yields a yellow, crystalline *platinochloride* of the composition $(\text{C}_{11}\text{H}_{17}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$; it melts at 224° with decomposition. The *aurochloride* melts at $159\text{--}161^\circ$, and the *picrate* is crystalline and melts at $156\text{--}159^\circ$. The *hydroxide* is obtained as a syrupy liquid, which absorbs carbonic anhydride from the air. W. J. P.

Action of Sulphur Chloride on Acetylacetone. By F. MAGNANI (*Gazzetta*, 23, ii, 415—419).—Sulphur chloride readily acts on acetylacetone with evolution of hydrogen chloride and development of heat. The product, which solidifies on pouring it into water, consists of *dithiodiacetylacetone*, $\text{CHAc}\cdot\text{S}\cdot\text{S}\cdot\text{CHAc}$; it crystallizes in yellowish laminae which melt at $89\text{--}90^\circ$, and has the normal molecular weight in boiling benzene. On boiling its alcoholic solution with hydroxylamine hydrochloride, it yields a *diisocazole*, $\begin{matrix} \text{N:CMe} \\ | \\ \text{O}\cdot\text{CMe} \end{matrix} > \text{C}\cdot\text{S}_2\cdot\text{C} < \begin{matrix} \text{CMe:N} \\ | \\ \text{CMe}\cdot\text{O} \end{matrix}$, which separates from light petroleum in white needles melting at $77\text{--}78^\circ$. On treating the thioacetone with phenylhydrazine a *di-pyrazole*, $\begin{matrix} \text{N} = \text{CMe} \\ | \\ \text{NPh}\cdot\text{CMe} \end{matrix} > \text{C}\cdot\text{S}_2\cdot\text{C} < \begin{matrix} \text{CMe} = \text{N} \\ | \\ \text{CMe} - \text{NPh} \end{matrix}$, is obtained, which crystallises in needles melting at $78\text{--}79^\circ$.

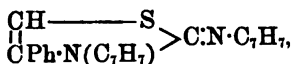
Small quantities of another *thio-derivative*, $\text{C}_{10}\text{H}_{14}\text{O}_4\text{S}_2$, which melts at 129° , are also formed during the interaction of sulphur chloride and acetylacetone. W. J. P.

Action of Halogenated Ketones on Thiocarbamides and on Ammonium Thiocarbamate. By G. MARCHESINI (*Gazzetta*, 23, ii, 437—443; compare Spica and Carrara, Abstr., 1892, 215; Mazzara, Abstr., 1893, i, 411). 2 : 5-Phenyldibenzileamidothiazole,



is prepared by heating unsymmetrical dibenzilethiocarbamide and bromacetophenone with acetone in a reflux apparatus; it crystallises in white needles melting at 106° , is soluble in alcohol or ether but not in water. On treatment with potash, it yields a *substance* which is soluble in ether, and melts at $85\text{--}86^\circ$.

On heating symmetrical dibenzilethiocarbamide with bromacetophenone, 1 : 2 : 5-benzilephenylbenzileimidothiazoline,



and its *hydrobromide*, $\text{C}_{23}\text{H}_{20}\text{N}_2\text{S}_2\text{HBr}$, are obtained. The base crystallises in needles melting at $66-67^\circ$, and is soluble in water, alcohol, or ether. The hydrobromide forms large, colourless, transparent, monosymmetric crystals which melt at 173° ; it is very soluble in alcohol, but sparingly so in water.

Ammonium thiocarbamate acts on chloracetone in boiling alcoholic solution with formation of 2 : 5-methylhydroxythiazole (compare Tscherniac, Abstr., 1892, 1425).
W. J. P.

Syntheses of Quinazolines. By C. PAAL, W. KRÜCKEBERG, F. KOCH, S. KÜTTNER, A. NEUBURGER, and K. STOLLBERG (*J. pr. Chem.*, [2], 48, 537-575; compare Abstr., 1890, 1443; 1892, 80; 1893, i, 438).—*Orthonitrobenzylparachloraniline*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$, from orthonitrobenzyl chloride and parachloraniline, crystallises in yellow prisms, melts at 85° , and dissolves in the usual organic solvents, but not in water (compare Abstr., 1891, 723). When heated with formic acid, it yields *orthonitrobenzylparachloroformanilide*,



which crystallises in colourless needles, melts at 110° , and is sparingly soluble in organic solvents.

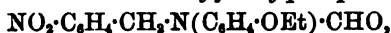
3'-Parachlorophenyl-dihydroquinazoline, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{N}=\text{CH} \\ \text{CH}_2 \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Cl} \end{array}$ is prepared by reducing the formanilide; it crystallises in white needles or laminæ, melts at 143° , and dissolves in most organic solvents and in warm mineral acids. The *stannochloride* (m. p. 189°), *hydrochloride*, *platinochloride* (m. p. 317°), *zincchloride* (m. p. 89°), *nitrate* (m. p. 156°), *acid sulphate* (m. p. 185°), *acid oxalate* (m. p. 168°), and *picrate* (m. p. 192°) are described.

3'-Parachlorophenyl-4'-ketodihydroquinazoline, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{N}=\text{CH} \\ \text{CO} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Cl} \end{array}$ is prepared from the preceding compound by oxidation with alkaline potassium permanganate. It crystallises in pale yellow, thin, stellate needles, melts at 177° , and dissolves in most organic solvents, but not in water. The *hydrochloride* melts at 192° , the *platinochloride* at 315° . By reduction with sodium, 3'-parachlorophenyl-dihydroquinazoline yields phenyltetrahydroquinazoline.

Orthamidobenzylparabromaniline, prepared by reducing the nitro-derivative (Abstr., 1893, 438) with zinc dust and acetic acid, crystallises in nearly white needles, melts at 104° , and dissolves in most organic solvents and mineral acids. When heated with formic acid, it yields *orthonitrobenzylparabromoformanilide*, which crystallises in colourless prisms, melts at 105° , and dissolves sparingly in the usual solvents. When reduced with tin and hydrochloric acid, the formanilide yields 3'-*parabromophenyl-dihydroquinazoline*, which crystallises in white laminæ or flat needles, melts at 142° , and is sparingly soluble in light petroleum, but freely soluble in hot alcohol; the *hydrochloride*, *platinochloride*, *aurochloride*, *acid oxalate*, and *picrate* (m. p. 202°) are described. The oxidation of the dihydroquinazoline with potassium

permanganate yields 3'-parabromophenyl-4'-ketodihydroquinazoline; this crystallises in large, pale yellow needles, melts at 174°, and dissolves sparingly in ether and light petroleum, but freely in alcohol, benzene, and glacial acetic acid; reduction with sodium converts it into 3'-phenyltetrahydroquinazoline.

Orthonitrobenzylparaphenetidine, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, from ortho-nitrobenzyl chloride and paraphenetidine, crystallises in large, red tables, melts at 52°, and is freely soluble in hot organic solvents, except light petroleum; by reduction with tin and hydrochloric acid, it yields 2'-paraphenetylindazole (Abstr., 1891, 724). The *hydrochloride* crystallises in needles and melts at 163°. When heated with formic acid, it yields *orthonitrobenzylformylparaphenetidine*,



which crystallises in colourless pyramids and tables, and melts at 96°.

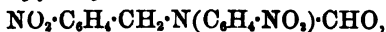
3'-Paraphenetyldihydroquinazoline, $\text{C}_6\text{H}_4\cdot\begin{matrix} \text{N}=\text{CH} \\ | \\ \text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OEt} \end{matrix}$ is obtained by reducing the above described formyl derivative; it crystallises in thin tables, melts at 109°, and dissolves in most solvents, except water and light petroleum. The *hydrochloride* (m. p. 207°), *stannochloride* (m. p. 132°), *platinochloride* (m. p. 206°), *aurochloride* (m. p. 179°), *acid oxalate* (with $\text{1H}_2\text{O}$; m. p., when anhydrous, 162°), and *picrate* (m. p. 194°) are described. The *keto-base*,



obtained by oxidising the quinazoline, crystallises in laminæ, and melts at 154°.

3'-Paraphenetyltetrahydroquinazoline is obtained by hydrogenating the dihydroquinazoline by sodium in alcohol; it crystallises in nacreous laminæ, and melts at 124°.

Orthonitrobenzylmetanitraniline, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, from ortho-nitrobenzyl chloride and metanitraniline, crystallises in yellow needles or laminæ, melts at 142—143°, and dissolves in most solvents except water and light petroleum. By treatment with formic acid, it yields *orthonitrobenzylformylmetanitraniline*,



which crystallises in grey prisms, melts at 140°, and dissolves sparingly in alcohol, ethylic acetate, and benzene, but more freely in glacial acetic acid, amyl alcohol, and chloroform. The corresponding *amido-*

phenyldihydroquinazoline, $\text{C}_6\text{H}_4\cdot\begin{matrix} \text{N}=\text{CH} \\ | \\ \text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \end{matrix}$, crystallises in white laminæ, melts at 147°, and becomes brown by oxidation in air; its *hydrochloride* (m. p. 230—232°), *stannochloride* (m. p. 264°), *platinochloride*, which melts with decomposition at 240°, *aurochloride*, *oxalate* (m. p. 157—159°), and *picrate* (m. p. 189°) are described; the *benzoyl-derivative*, $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COPh}$, obtained by heating the dihydroquinazoline with benzoic chloride, is a crystalline powder, and melts at 82°. When the dihydroquinazoline is heated with methylic iodide in methylic alcohol, *metamethylamidophenyldihydroquinazoline methiodide*,

$C_6H_4 < \begin{matrix} NMeI:CH \\ CH_2-N \cdot C_6H_4 \cdot NHMe \end{matrix}$, separates as a hydriodide in the form of stellate crystals which melt at 153° ; the free base crystallises in small prisms, and melts at 185° .

Metamidophenyltetrahydroquinazoline, $C_6H_4 < \begin{matrix} NH \cdot CH_2 \\ CH_2 \cdot N \cdot C_6H_4 \cdot NH \end{matrix}$, obtained by hydrogenating the dihydroquinazoline, crystallises in laminae, and melts at 156° ; its *hydrochloride*, which melts with decomposition at 210° , *stannochloride*, *platinochloride*, and *aurochloride* are described.

Orthonitrobenzylallylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH \cdot CH_3$, from orthonitrobenzyl chloride and allylamine, is a colourless oil, soluble in most organic solvents and in mineral acids; it cannot be distilled. Its *hydrochloride* (m. p. $136-137^\circ$) and *platinochloride* (m. p. 163°) are described. When heated with formic acid, it yields *orthonitrobenzylformallylamine*, a viscid, yellow oil, which cannot be distilled, and dissolves in organic solvents and concentrated mineral acids. By reduction the base yields 3'-allyldihydroquinazoline, a bitter, yellowish oil, having the odour of conine, and boiling with decomposition at $280-290^\circ$; its *hydrochloride* (m. p. 165°), *hydrobromide* (m. p. 168°), *perbromide*, *hydriodide* (m. p. 199°), *platinochloride* (m. p. $191-192^\circ$), *acid oxalate* (m. p. 172°), and *picrate* (m. p. $172-173^\circ$) are described. The *tetrahydroquinazoline* is a colourless, easily oxidised oil, which boils at $270-272^\circ$; its *acid oxalate* melts at 164° .

A. G. B.

Action of Hydrocyanic acid on Phenylhydrazine. By E. FISCHER and F. MÜLLER (*Ber.*, 27, 185—187).—The compound obtained by the author (*Ber.*, 22, 1933) by warming phenylhydrazine with hydrocyanic acid is found to be identical with the cyanophenylhydrazine, $(C_6H_5N_3)_2$, described by Senf. The authors have prepared from it bisphenylmethyltriazole, bisphenylethyltriazole, and bisphenylpropyltriazole, as described by Bladin.

Bisphenyltriazole, $\begin{matrix} CH:N \\ NPh \cdot N \end{matrix} > C \cdot C < \begin{matrix} N:CH \\ N \cdot NPh \end{matrix}$, is obtained by heating cyanophenylhydrazine with formic acid. It melts at $277-278^\circ$ (corr.) and dissolves in hot dilute and concentrated mineral acids.

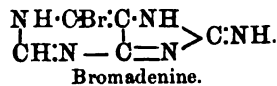
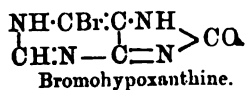
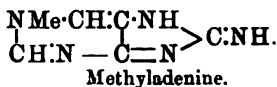
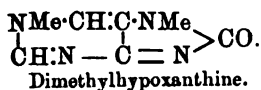
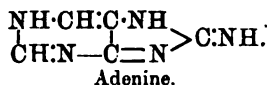
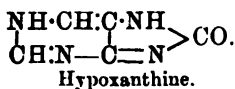
E. C. R.

Adenine and Hypoxanthine. By M. KRÜGER (*Zeit. physiol. Chem.*, 18, 423—458, 459—472).—In continuation of previous work (*Abstr.*, 1892, 219, 890; 1893, 736), the properties of a number of other preparations from adenine and hypoxanthine are described. In the first of the present papers the method of preparation, analysis, metallic compounds, solubilities, crystalline form, reactions, and decomposition products of the following substances are given:—Benzyladenine, $C_6H_4N_6 \cdot C_6H_5$; *disbenzyladenine*, $C_6H_4N_6(C_6H_5)_2$, melting at 171° ; methyladenine methiodide, an additive product; *lead adenine*, $C_6H_4N_6Pb$; *diethylhypoxanthine ethiodide*; *methyladenine*; *dimethylhypoxanthine*; *ethyladenine*; *isoamyladenine* melting at $148-150^\circ$; and *isoamylhypoxanthine*.

Bromohypoxanthine can be obtained in a similar way to the corresponding adenine compound.

The second paper treats of the constitution of the adenine and hypoxanthine molecules. It is pointed out that adenine, like xanthine, guanine, and caffeine, gives a monobromo-derivative, the hydrobromide of which will combine with four extra atoms of bromine. Hypoxanthine has the same property. The existence of dimethylhypoxanthine, which agrees in all its properties with caffeine, shows that hypoxanthine and adenine contain two imido-groups replaceable by metals and alkyls. Adenine contains, indeed, a third imido-group, corresponding with the oxygen atom of hypoxanthine. By the oxidation of bromadenine and bromohypoxanthine with hydrochloric acid and potassium chlorate, alloxan, and large quantities of urea are produced. Hence adenine and hypoxanthine contain an alloxan nucleus; whether a carbamide nucleus is present in addition is doubtful. On decomposing hypoxanthine and adenine by concentrated hydrochloric acid, these products are obtained qualitatively in the same way as by the decomposition of xanthine and uric acid.

By the action of concentrated hydrochloric acid on methyladenine, the methyl group is eliminated as methylamine. By the same treatment, dimethylhypoxanthine yields methylamine and methylglycocine. From these and other considerations of similar nature, the following constitutional formulæ are suggested :—



W. D. H.

Isoconline. By A. LADENBURG (*Bull. Soc. Chim.*, [3], 9, 801—802; compare *Abstr.*, 1893, i, 442).—Attempts to split hydroquinoline, a substance containing “asymmetric nitrogen” (*loc. cit.*), but not asymmetric carbon, into optically active modifications by fractional crystallisation of the tartrate have proved unsuccessful. This is a strong argument against the “asymmetric nitrogen” hypothesis, a point which Simon, in a critical abstract of the former paper, has contested. JN. W.

Some New Tropeïnes. By A. PETIT and M. POLONOVSKY (*J. Pharm.*, [5], 28, 529—581).—In some cases alkyl salts can be substituted with advantage for the corresponding acids in the preparation of tropeïnes by Ladenburg's method.

Benzilotropeine, $C_8H_{14}NO \cdot CO \cdot CPh_2OH$, crystallises in hard prisms. It is soluble in alcohol or ether, slightly soluble in water, and is not hygroscopic. It is a strong base with a bitter taste and yields stable, crystalline salts.

Phenylcarbamotropeine, $C_8H_{14}NO \cdot CO \cdot NHPh$, is produced by heating phenylic isocyanate with a solution of tropine in benzene on the water bath for some minutes. Diphenylcarbamide is formed in small quantity at the same time. This urethane is insoluble in water, sparingly soluble in cold benzene, and soluble in alcohol or ether. Its hydrochloride is precipitated by an excess of acid.

Succinotropeine is obtained as an oil. Its aurochloride crystallises in yellow needles melting at 167° .
W. T.

Caffearine. By P. PALLADINO (*Chem. Centr.*, 1893, ii, 721; from *Apoth. Zeit.*, 8, 443—444).—This alkaloid was obtained by a lengthy process from coffee, and crystallises in needles readily soluble in water and alcohol. The hydrochloride, $C_{14}H_{16}N_2O_4 \cdot HCl + H_2O$, also crystallises in needles.
C. F. B.

Nucleic acid. By A. KOSSEL (*Chem. Centr.*, 1893, ii, 649—650; from *Centr. Med. Wiss.*, 1893, 497—499).—The author replies to Liebermann and v. Bittó (see this vol., i, 155), that their analysis of the baryta precipitate does not fulfil the requirements of a scientific research either in its execution or in its results. The author also points out that he has not in any particular adopted the views of Liebermann as to the nucleins. The two views are, in fact, fundamentally different. Liebermann's observations on the formation of xanthine substances do not in any way affect Kossel's view that the nuclein bases are formed by the decomposition of the molecule of nuclein or nucleic acid.
A. H.

Albumin of the Hen's Egg. By E. SALKOWSKI (*Chem. Centr.*, 1893, ii, 532; from *Centr. med. Wiss.*, 31, 513—515).—If a solution of hen's egg albumin is carefully neutralised with dilute acetic acid, and the solution precipitated by boiling, a hitherto unobserved albumose is found in the filtrate. The latter is isolated by concentrating the solution and precipitating with absolute alcohol. It is readily soluble in water, gives the biuret reaction, is precipitated by ammonium sulphate, tannin, and a hydrochloric acid solution of phosphotungstic acid, but not by acetic acid or sodium chloride. When the solution is evaporated on the water bath, it passes into an insoluble anhydride which swells up in water and is insoluble in dilute acids, concentrated hydrochloric acid, and glacial acetic acid. The anhydride dissolves in nitric acid of sp. gr. 1.2, with a yellow colour which changes to orange on the addition of alkali. It swells up in dilute ammonia, partially dissolving at the same time; it dissolves readily in dilute aqueous soda, and is not precipitated from the solution by acetic acid.

The fermentable sugar which the albumin contains is glucose.

H. G. C.

Constitution of Vegetable Proteids. By E. FLEURENT (*Compt. rend.*, 117, 790—793).—Gluten, gluten-casein, gluten-fibrin, legumin,

and vegetable albumin were heated with barium hydroxide solution, as in Schützenberger's experiments with proteids of animal origin. The products are qualitatively the same, and the non-volatile products likewise amount to about 95 per cent. of the original substance, but the ratio of the ammonia to the barium oxalate and carbonate is very different. In the case of proteids of the gluten group it is higher, and in the case of legumin and vegetable albumin it is lower, than with proteids of animal origin. Vegetable casein and vegetable fibrin give identical results.

It is known that the splitting up of gluten yields glutamic acid, whilst legumin and vegetable albumin yield aspartic acid, and it would seem that, as Schützenberger suggests, the disproportion between the ammonia and the insoluble barium salts is due to the existence of an amide similar to asparagine in the molecule of the vegetable proteid. Glutamic and aspartic acids are liberated and afterwards decompose, yielding a further quantity of barium carbonate. This view is supported by the fact that in the case of gluten the proportions of ammonia and oxalic acid remain constant, but the proportion of barium carbonate increases with the duration of the reaction. The same phenomenon is observed in the case of vegetable albumin and legumin. In the fixed residue, the ratio of carbon to hydrogen, C_8H_{12} , is identical with that found by Schützenberger in the case of animal compounds. It is clear, however, that the constitution of vegetable proteids is different from that of animal proteids.

C. H. B.

Albumose. By H. SCHRÖTTER (*Monatsh.*, 14, 612—623).—The author has prepared from Witte's commercial peptone an albumose, which is soluble in and crystallises from alcohol, is practically ashless, and furnishes a hydrochloride of constant composition. The method employed is as follows:—The peptone is boiled with absolute methylic alcohol in a reflux apparatus, by which soluble impurities are removed. The residue is dissolved in water containing sulphuric acid, and is treated with zinc dust and sulphuric acid, the latter being added a little at a time. After remaining several days, and being warmed for four hours in a water bath, the solution is filtered, the sulphuric acid removed by excess of baryta, the clear solution saturated with carbonic anhydride, concentrated, again filtered, and eventually evaporated to dryness in a vacuum over sulphuric acid. The residue is exhausted with hot methylic alcohol, the extract concentrated, and the albumose precipitated with absolute ether. In order to obtain an ashless preparation, the albumose is subjected to treatment by Paal's process (compare *Abstr.*, 1892, 895—897). The albumose dissolves readily in water and methylic alcohol; is sparingly soluble in cold alcohol; gives the biuret reaction characteristic of albumoses and peptones; is precipitated by tannin, mercuric chloride, ammonium sulphate, and sodium chloride; and contains, after allowing for 0.22—0.5 per cent. of ash, C 50.5—51.3, H 6.4—7.0, N 16.5—17.1, S 1.1 per cent. The hydrochloride contains C 47.2—48.5, H 6.5—7.3, N 14.6—14.7, S 0.9—1.1, HCl 10.5—11.0 per cent. The molecular weight of the albumose, as determined by

Raoult's method, in aqueous solution, was found to be between 587 and 714, whereas, if it be supposed that the molecule contains at least 1 atom of sulphur, the molecular weight, as deduced from analysis above, cannot be less than 2,000. In behaviour and composition the substance closely resembles the protalbumose described in *Beilstein's Handbuch*, 3, 1304. On benzoylation, the albumose gives two products, of which one (C 60·8, H 5·8—6·0, N 12·6—12·8, S 0·9 per cent.) is crystalline, insoluble in alcohol, and yields on hydrolysis 19·7 per cent. of benzoic acid; and the other (C 59·3—59·9, H 6·1—6·4, N 12·3—11·9 per cent.) is soluble in cold alcohol, contains apparently no sulphur, and yields on hydrolysis 17·5—18·6 per cent. of benzoic acid.

G. T. M.

Casein and the Organic Phosphorus of Casein. By A. BÉCHAMP (*Compt. rend.*, 117, 1085—1088).—In order to detect and estimate phosphorus (and sulphur) in casein, a known weight of the dry compound is mixed with a standard solution of bismuth nitrate, evaporated to dryness, dried at 110°, and afterwards heated to dull redness. The difference between the total weight of the residue and the weight of the bismuth oxide gives the weight of the sulphuric and phosphoric acids.

Carefully purified casein of different preparations contains from 0·74 to 0·76 per cent. of phosphorus and 0·04 to 0·046 per cent. of sulphur. The insoluble product formed by the action of heat on casein contains 0·44 to 0·46 per cent. of phosphorus, and it is clear that phosphorus is an essential constituent of casein, and is present in organic combination.

Since casein contains both sulphur and phosphorus, it presents the first example of an immediate principle containing six elements.

C. H. B.

Synthesis of Hæmoglobins. By H. BERTIN-SANS and J. MOITESSIER (*Bull. Soc. Chim.*, [3], 9, 721).—Hæmoglobins have been formed by combining hæmatins and proteid substances obtained from the blood of sheep and fowls, both when the two constituents have been obtained from the blood of one animal species and when each constituent has had its origin in a different one of the three sources—cattle, sheep, and fowls.

W. T.

Displacement of the Carbonic Oxide in Carboxyhæmoglobin by Oxygen. By H. BERTIN-SANS and J. MOITESSIER (*Bull. Soc. Chim.*, [3], 9, 722).—The displacement of carbonic oxide from carboxyhæmoglobin by aëration may be rapidly shown by a comparison of the spectra of two portions of blood saturated with carbonic oxide, after passing a rapid current of air through one and subsequently treating both with a solution of soda containing a little ammonium sulphide. The aërated sample shows the spectrum of hæmochromogen together with the much weakened spectrum of carboxyhæmoglobin; the other only shows the hæmochromogen spectrum after about an hour.

W. T.

Organic Chemistry.

Action of Sulphuric acid on Wood Charcoal. By A. VERNEUIL (*Compt. rend.*, 118, 195—198).—When wood charcoal is heated with concentrated sulphuric acid, the residue in the flask contains, together with other acids which are under investigation, mellitic acid and benzenepentacarboxylic acid identical with that obtained by Friedel by the oxidation of pentamethylbenzene; 1400 grams of ordinary sulphuric acid was heated with 100 grams of carbon, the process being continued until only from 90 to 100 grams of residue remained in the flask. The temperature of the reaction was about 280°, but rose towards the end to about 300°, a rapid evolution of gas being maintained in order to ensure that the water formed was expelled with the carbonic and sulphurous anhydrides.

When the residue is treated with water, a dark brown solution is formed, and a black, insoluble coagulum remains, showing no trace of the original structure of the charcoal. It is soluble in alkalis and in concentrated sulphuric acid, and is under investigation. The strongly acid solution is mixed with just sufficient barium chloride to precipitate the sulphuric acid, filtered, and evaporated to dryness, when a brown, amorphous, strongly acid residue is left, equal in weight to about 20 per cent. of the original carbon. When this residue is dissolved in water, saturated with ammonia, filtered and concentrated, ammonium mellitate separates in quantity equal to about 4 per cent. of the original carbon.

The mother liquor is evaporated with a slight excess of barium hydroxide, and the barium salts are dissolved in hydrochloric acid, and fractionally precipitated with barium hydroxide solution. The first fraction carries down most of the colouring matter, whilst the next fraction is crystalline, and consists of barium benzenepentacarbonylate, which can be recrystallised from hydrochloric acid in the form of an acid salt.

C. H. B.

Substitution in the Aliphatic Series. By A. HERZFELDER (*Ber.*, 27, 489—490).—The author has made the conclusions given in this vol. (i, 1) yet more sure, by affording additional confirmation of the facts from which they are drawn. He proves that the hexabromhexane, heptabromheptane, and octobromoctane are really derivatives of the hexane, heptane, and octane, from which they are respectively obtained on treatment with bromine and a little iron wire, for he shows that these hydrocarbons are regenerated from them when they are reduced with sodium in alcoholic solution.

C. F. B.

Tetramethylethylene Nitrosochloride. By J. THIELE (*Ber.*, 27, 454—456).—The author gives directions for preparing pinacone by a modification of Friedel's method. When pinacone hydrate is melted in a beaker, and mixed with hydrobromic acid, saturated at 0° (5 parts), crystals of tetramethylethylene bromide are deposited after 48 hours;

these are converted into tetramethylethylene (b. p. 73°), when treated with glacial acetic acid and zinc dust.

The *nitrosochloride*, $\text{CMe}_2\text{Cl}\cdot\text{CMe}_2\text{NO}$, prepared by the action of nitrosyl chloride, or better that of sodium nitrite and hydrochloric acid, on tetramethylethylene, is a blue powder, having a camphor-like penetrating odour; it melts at 121° with slight evolution of gas, volatilises in part undecomposed when boiled with water, and is only very slowly hydrolysed by alcoholic alkali in the cold. It does not give Liebermann's reaction, liberates iodine from potassium iodide in the cold, and yields silver chloride when treated with alcoholic silver nitrate.

A. R. L.

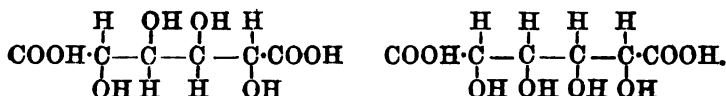
Gelatinous Silver Cyanide. By L. K. FRANKEL (*Chem. Centr.*, 1893, ii, 965; from *Proc. Chem. Sect. Frank. Inst.*, 1893, August).—With the intention of reducing the salt, some silver chloride was fused with potassium cyanide, the melt boiled with water, and the whole allowed to remain over night. In the morning, the beaker was found to be filled with a transparent, gelatinous precipitate, similar to, but denser than, aluminium hydroxide. On filtering and drying, the precipitate shrank together considerably. It was soluble in ammonia, and was reprecipitated from this solution by nitric acid. When heated, it did not fuse, but decomposed, metallic silver being left. It gave the cyanogen reactions, but contained 5 per cent. less silver than pure argentic cyanide does. The author believes the substance to have been a gelatinous form of silver cyanide, but has not succeeded in reproducing it.

L. T. T.

Preparation of Ferricyanides. By G. KASSNER (*Chem. Zeit.*, 17, 1712—1713).—The author has previously described a method for the technical preparation of potassium ferricyanide by the action of carbonic anhydride on a mixture of potassium ferrocyanide and calcium plumbate (Abstr., 1890, 352). The separation of potassium carbonate from potassium ferricyanide is attended with some difficulty; he suggests, therefore, the addition to the mixed potassium salts, after the oxidation, of sufficient calcium ferricyanide to decompose the whole of the potassium carbonate; if the liquids are heated, the precipitated calcium carbonate rapidly subsides. Calcium ferricyanide is readily prepared from calcium ferrocyanide by the action of calcium plumbate and carbonic anhydride under pressure at the ordinary temperature; the resulting solution can be used directly. For the preparation of the solid salt, it must be evaporated under reduced pressure, otherwise the calcium ferricyanide will be partially decomposed, as it is less stable than potassium ferricyanide.

J. B. T.

Configuration of Rhamnose and Galactose. By E. FISCHER and R. S. MORRELL (*Ber.*, 27, 382—394).—The configuration of the sugars derived from mannitol has, for the most part, been cleared up during the past few years, but very little is known with regard to the configuration of those derived from dulcitol. Mucic acid is known to contain an optically inactive system, but both the following formulæ fulfil this condition.



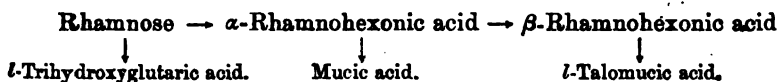
The investigation of rhamnose has unexpectedly led to the solution of the problem, inasmuch as this sugar, which belongs to the mannitol group, has been converted into mucic and talomucic acids, which are derived from dulcitol.

By the oxidation of rhamnose with nitric acid, Will and Peters (Abstr., 1889, 952) obtained the same trihydroxyglutaric acid that is formed from arabinose, the configuration of which is known. By the action of hydrogen cyanide on rhamnose, and subsequent hydrolysis, it is converted into rhamnohexonic acid, which must have the structure—

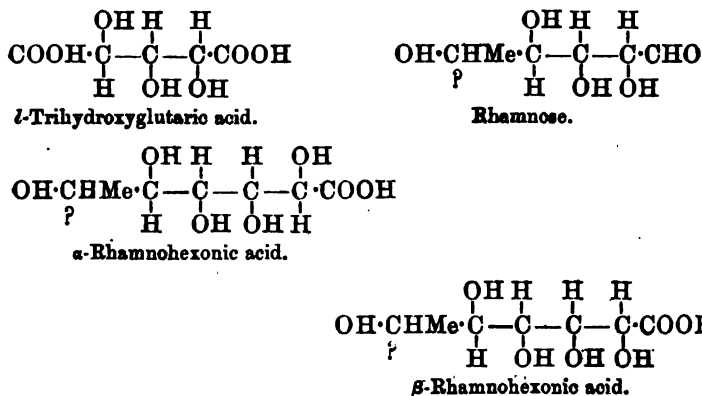


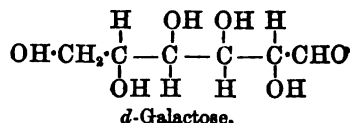
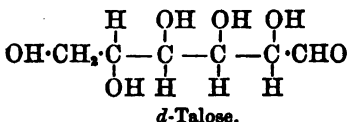
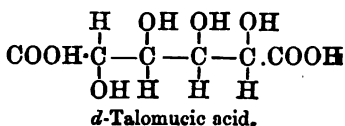
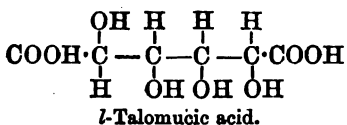
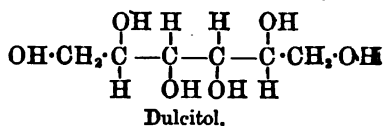
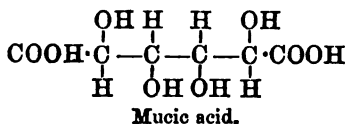
On oxidation, it yields large quantities of mucic acid, and, when heated with pyridine, rhamnohexonic acid is converted into a stereo-isomeric compound, which must, according to previous experience, differ from the first acid simply in the arrangement of the atoms around the carbon atom denoted by an asterisk in the above formula. The new acid, on oxidation, yields the optical isomeride of talomucic acid, which is itself obtained by the oxidation of *d*-galactose, and must, therefore, be termed *d*-talomucic acid, the new compound being the *L*-derivative.

The above changes are represented by the following scheme.



The configuration of all these compounds may be derived from the known configuration of *L*-trihydroxyglutaric acid in the following manner.





In the case of rhamnose and the rhamnohexonic acids, the configuration of the hydrogen and hydroxyl in combination with the carbon atom marked ? is still doubtful, and it is therefore uncertain whether they are derived from *l*-mannose or *l*-gulose.

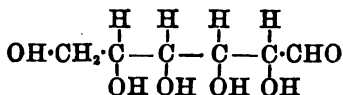
The preparation of α -rhamnohexonic acid has already been described (Abstr., 1888, 806, 933, 1049). Its *phenylhydrazide* dissolves in 72 parts of water at 17°, and the *cadmium* salt, $(\text{C}_7\text{H}_{13}\text{O}_7)_2\text{Cd}$, crystallises in colourless, lustrous plates, and dissolves in 271 parts of water at 14°, and in about 20 parts at the boiling point. The *brucine* salt forms nodular aggregates of crystals, and melts at 120—123°. When treated with nitric acid of sp. gr. 1.2 at 40—45°, the chief product is mucic acid.

When heated with pyridine and water at 150—155°, α -rhamnohexonic lactone is converted partially into the optically isomeric β -rhamnohexonic lactone. In order to separate the two compounds, they are converted first into the barium salts and subsequently into the cadmium salts, the latter salt of the β -acid being readily soluble in water, whereas that of the α -acid is very slightly soluble. The solution of the β -cadmium salt is precipitated by hydrogen sulphide, and the solution of the free acid converted into the *brucine* salt, which forms spherical, crystalline aggregates, and melts at 114—118°. The free acid is obtained from the latter by boiling with baryta water, and decomposing the barium salt with sulphuric acid; on evaporation, the filtered solution yields a syrup, consisting chiefly of the lactone, which solidifies after a time, and crystallises from acetone in crusts of colourless, lustrous plates. It melts and decomposes at 134—138°; it is dextrorotatory, $[\alpha]_D$ being +43.34°, and remaining constant. The *phenylhydrazide* forms slender, lustrous plates, sinters at 160°, and melts at 170° with slight evolution of gas.

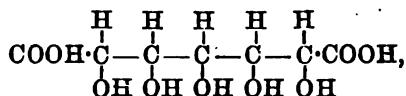
If the β -lactone is heated with pyridine, it is partly reconverted into the α -derivative; on reduction, it yields a sugar, which was not obtained in sufficient quantity for isolation, but which is converted by phenylhydrazine into the same rhamnohexosazone as α -rhamnohexose, thus proving that these two acids differ only in the arrangement of the atoms combined with the carbon atom next to the carboxyl group.

With nitric acid, β -rhamnohexonic lactone yields *l*-talomucic acid: To isolate this acid, it was converted into the *calcium* salt, which, after purification, has the composition $C_6H_8O_6Ca$. The free acid has the same melting point, crystalline form, and solubility as the *d*-talomucic acid, but is *laevorotatory*, $[\alpha]_D = -33.9^\circ$. The *phenylhydrazide* crystallises in lustrous, pale yellow plates, and very closely resembles the *d*-derivative; it melts at 185° with decomposition, and, unlike mucic acid phenylhydrazide, dissolves readily in boiling water. *l*-Talomucic acid may be converted into mucic acid in the manner already described for the *d*-compound (Abstr., 1892, 299).

The configuration of *d*-galactose deduced from the foregoing experiments receives further confirmation from the fact that this sugar, on treatment with hydrogen cyanide and subsequent hydrolysis, yields, in addition to the carboxylic acid described by Kiliani, a stereoisomeric compound, which, like the latter, is optically active. This would be impossible if *d*-galactose had the formula



or its image, as one of the two pentahydroxypimelic acids must then have the configuration



and would be optically inactive.

H. G. C.

Compounds of the Sugars with Iron. By F. EVERS (*Ber.*, 27, 474—475).—*Iron sucrate*, containing about 48.5 per cent. of iron, is obtained as a crystalline, reddish-brown powder by pouring a solution of cane sugar and ferric chloride into a slight excess of aqueous sodium hydroxide; it dissolves to the extent of about 95 per cent. in cane-sugar solution, leaving a residue of ferric hydroxide.

Iron maltosate was prepared in the same way; it is a brown, amorphous substance, and is not mixed with free ferric hydroxide, for it dissolves entirely in maltose solution. It contains about 32 per cent. of iron, corresponding with the formula $2Fe_2O_3, C_{12}H_{22}O_{11} + 2H_2O$.

C. F. B.

Crystalline Amido-derivatives of the Carbohydrates. By C. A. LOBRY DE BRUYN and A. P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 12, 286—289).—Ledderhose obtained so-called glucosamine hydrochloride by boiling chitin with hydrochloric acid; this base has also been studied by Tiemann (Abstr., 1884, 724; 1886, 329). Furthermore, Fischer obtained isoglucosamine by the reduction of ordinary glucosazone (Abstr., 1886, 933; 1888, 39). The direct transformation of the carbohydrates into amido-derivatives has not heretofore been observed.

In studying the two isomeric pentacetyl derivatives of glucose, the

authors observed that crystalline needles of glucosamine are slowly formed when the acetyl compounds are treated with alcoholic ammonia.

Further experiment showed that glucose itself is incapable of dissolving in ethyl alcoholic ammonia, but it dissolves freely in methyl alcoholic ammonia; after some weeks, the rotatory power of the solution gradually becomes less, and crystalline aggregates of the glucosamine last mentioned are deposited. This compound is not identical with that obtained from chitin.

Milk sugar and galactose are also insoluble in ethyl alcoholic ammonia, but dissolve in methyl alcoholic ammonia, forming crystalline osamines. The lactosamine seems to be an aldehyde-ammonia.

Fructose (levulose) dissolves in both ethyl alcoholic and methyl alcoholic ammonia, giving rise to a crystalline and an amorphous compound, which are probably isomeric, containing the same percentage of nitrogen as glucosamine.

The stability of these bases is very different: thus, glucosamine and lactosamine lose nitrogen as ammonia when boiled with N/10 sulphuric acid, and may be analysed by titration, whereas fructosamine is not decomposed under these circumstances.

It may be mentioned that this paper is only a preliminary communication on the subject, and no analytical data are given.

A. R. L.

Carbohydrates of Yeast. By E. SALKOWSKI (*Ber.*, 27, 497—502).—A gum was obtained from German yeast, as free as possible from starch, by heating 500 grams of the yeast with 5 litres of 3 per cent potash, boiling for half an hour, siphoning off the liquid after a time, and heating it with 750 c.c. of Fehling's solution on the water bath. A copper compound of the gum was precipitated in bluish-white flakes; it was dissolved in water with the addition of a little hydrochloric acid, and the gum precipitated by adding alcohol; it was further purified by dissolving it in water and reprecipitating with alcohol, finally washing with alcohol and with ether. Thus prepared, it forms a fine, white powder, having the composition $C_{13}H_{22}O_{11}$, and specific rotation $[\alpha]_D = +90.1^\circ$. It greatly resembles gum arabic, but, unlike the latter, it gives, in 1 per cent. aqueous solution, an immediate precipitate with Fehling's solution, but no turbidity when an equal volume of 1.12 per cent. hydrochloric acid and then 5 per cent. phosphotungstic acid are added. Acids convert the gum into a sugar; the latter is feebly dextrorotatory, reduces Fehling's solution, and is capable of undergoing fermentation. The gum is contained in the yeast to the extent of 2 per cent., that is, 7 per cent. of the dried material. No pentoses are present in the yeast.

C. F. B.

Thermal Constants of Some Polyatomic Bases. By A. COLSON and G. DARZENS (*Compt. rend.*, 118, 250—253).—*Ethylenediamine*: Specific heat. 0.84 between 12° and 45° ; heat of dissolution at $15^\circ = +7.6$ Cal. Heat of neutralisation by hydrochloric acid, first equivalent $= +12.50$ Cal.; second equivalent, $+11.02$ Cal.; total $= 23.52$ Cal. Heat of dissolution of the normal salt $= -7.55$ Cal. at about 15° .

Litmus and methyl-orange indicate the formation of the normal

salt, but with phenolphthalein the colour change takes place at a point intermediate between the normal salt and the basic salt. The existence of two basicities of not quite equal value is made evident by the thermochemical results only.

Quinine :—Heat of dissolution of the normal sulphate at about $11^{\circ} = -6.7$ Cal.; heat of neutralisation of the base by sulphuric acid in molecular proportion, + 15.5 Cal.

Basic quinine sulphate is generally supposed to have the composition $Q_2, H_2SO_4 + 7H_2O$, but analysis of a well crystallised specimen indicated the presence of $8H_2O$. Quinine contains a feeble basic function analogous to that of quinoline and a strong basic function similar to that of the amines of the ethylic, allylic, or piperidic series.

C. H. B.

Fractional Fermentation. The Amyloïns (Maltodextrins).

By G. H. MORRIS and J. G. WELLS (*Trans. Inst. Brew.*, 5, 133—172).

—Starch transformations and beer worts of known optical activity and cupric reducing power were fermented with yeast, fractions being removed at intervals and the amounts of alcohol estimated in them; the alterations in optical activity and cupric reducing power were also noted. Practically the whole of the malt extract sugars are fermented in the first 48 hours, and, after this, the three estimations give identical results as to the amount of fermented matter calculated as maltose. Subsequently, that is, during the secondary fermentation, when all the free maltose has been removed, the quantity of alcohol formed and the optical activity indicate a larger amount of maltose than does the cupric reducing power. The authors assume that the amount of copper oxide reduced by any amyloïn is proportional to the quantity of combined maltose which it contains, whilst the amount of alcohol produced corresponds with the free maltose resulting from the hydrolysis of the amyloïns by the yeast.

Interesting results were obtained with two varieties of pure yeast, namely, Saaz yeast and Froberg yeast; the former ferments about one-seventh less matter than the latter. The relative attenuations are uninfluenced by the quantity of yeast employed, the temperature, and degree of aëration of the wort, and they remained constant for six months. The addition of diastase caused a further fermentation in both cases. When a beer fermented to its fullest extent with Saaz yeast is sown with Froberg yeast, fermentation recommences, and continues to the point it would have attained had the latter yeast been employed from the commencement. When crystallised maltose is added to a beer fermented to its lowest point by Saaz yeast, fermentation again sets in and continues until all the maltose is fermented. It is further shown that whilst Saaz yeast is incapable of fermenting anything beyond free maltose (probably on account of the absence of diastatic power), Froberg yeast readily ferments the amyloïns of the low type, to which class the authors believe Lintner's so-called isomaltose to belong.

A. R. L.

Hydroxylamine and its Homologues. By C. KJELLIN (*Ber.*, 27, 587—588).—The author refers to a recent paper by Brühl on this

subject (this vol., i, 9), and points out that the results published simultaneously in his own paper (*loc. cit.*) were obtained independently of Brühl. β -Ethylhydroxylamine is much more stable than Brühl states, and, when pure, may be kept for several days without undergoing decomposition. J. B. T.

Condensation of Isovaleraldehyde with Acetone. By P. BARBIER and L. BOUVEAULT (*Compt. rend.*, 118, 198—201).—A mixture of isovaleraldehyde 100 parts, acetone 100 parts, sodium hydroxide solution (1:10) 100 parts, water 600 parts, is allowed to remain at the ordinary temperature with frequent agitation for three days; the supernatant layer of liquid is then separated, dried by means of fused sodium acetate, and fractionated. The greater part passes over between 170° and 190°, and obstinately retains water, which is removed by boiling it for a short time with acetic anhydride and again fractionating.

The purified product is a colourless mobile liquid of agreeable odour resembling that of amylic acetate; it has the composition $C_8H_{14}O$, boils at 180° under a pressure of 750 mm., sp. gr. at 0° = 0.8580; refractive index at 17.8 for $\lambda 645 = 1.4425$ and for $\lambda 526 = 1.4581$.

With a hydrogen alkali sulphite, after long contact, it yields a crystallised product; when treated in the cold with a mixture of sodium hydroxide, sodium hypobromite, and potassium iodide it yields iodoform. It is also decomposed by the hypobromite alone but does not seem to yield bromoform. With Crismer's reagent it yields a liquid oxime, boiling, with slight decomposition, at 225—230° under ordinary pressure; this oxime yields a sodium salt insoluble in concentrated sodium hydroxide solution, and an oily benzoyl-derivative. When heated with alcohol and sodium, it yields a very small quantity of methylhexylcarbinol, together with a large quantity of a liquid substance of high boiling point, which seems to be the corresponding pinacone.

When oxidised with chromic mixture, the compound $C_8H_{14}O$ yields nothing but isovaleric acid, and, therefore, it must be regarded as *iso-amyliideneacetone*, $CHMe_2CH_2\cdot CH\cdot CH\cdot COMe$. It differs in its properties from the compound obtained by Wallach by the action of heat on cinoleic anhydride, and therefore the latter is not isoamyliideneacetone as Tiemann and Semmler supposed, but must have a different constitution, as Wallach originally stated. C. H. B.

Heat of Combustion of Fatty Acids. By F. STOHMANN, C. KLEBER, H. LANGBEIN, and P. OFFENHAUER (*J. pr. Chem.*, [2], 49, 99—129).—The authors have redetermined the thermal values for the fatty acids (*Abstr.*, 1886, 296). They describe the new method, and give the following values for solid acids (see next page).

It will be noted that the only two isomeric acids in the list have practically the same heat of formation. Formic acid should possess greater energy than acetic acid, for the difference between their heats of combustion is smaller than it should be; the same has been

observed in the case of oxalic acid in comparison with malonic acid. In their other relationships these two acids stand apart from the rest of those in their series, indicating that they are more energetic compounds (compare Ostwald, *Lehrbuch*, [2], 2, i, 650).

	Heat of combustion. Cal.	Difference. Cal.	Heat of formation. Cal.
Formic acid, CH_2O_2	59.0		104.0
Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$	206.7	147.7	119.3
Propionic acid, $\text{C}_3\text{H}_6\text{O}_2$	364.0	157.3	125.0
Normal butyric acid, $\text{C}_4\text{H}_8\text{O}_2$	520.4	156.4	131.6
Normal valeric acid, $\text{C}_5\text{H}_{10}\text{O}_2$	677.2	156.8	137.8
Isobutyrlacetic acid, $\text{C}_5\text{H}_{10}\text{O}_2$	832.2	{ 155.0 }	{ 145.8 }
Diethylacetic acid, $\text{C}_5\text{H}_{12}\text{O}_2$	832.3	{ 155.1 }	{ 145.7 }
Ethylpropylacetic acid, $\text{C}_7\text{H}_{14}\text{O}_2$..	988.8	156.5	152.2
Dipropylacetic acid, $\text{C}_8\text{H}_{16}\text{O}_2$	1145.0	156.2	159.0
Heptylacetic acid, $\text{C}_8\text{H}_{16}\text{O}_2$	1302.3	157.3	164.7
Normal capric acid, $\text{C}_{10}\text{H}_{20}\text{O}_2$	1458.3	156.0	171.7
Undecylic acid, $\text{C}_{11}\text{H}_{22}\text{O}_2$	1615.9	157.6	177.1
Lauric acid, $\text{C}_{12}\text{H}_{24}\text{O}_2$	1771.8	155.9	184.2
Myristic acid, $\text{C}_{14}\text{H}_{28}\text{O}_2$	2085.9	157.0×2	196.1
Palmitic acid, $\text{C}_{16}\text{H}_{32}\text{O}_2$	2398.4	156.2×2	209.6
Stearic acid, $\text{C}_{18}\text{H}_{36}\text{O}_2$	2711.8	156.7×2	222.2
Arachidic acid, $\text{C}_{20}\text{H}_{40}\text{O}_2$	3025.8	157.0×2	234.2
Behenic acid, $\text{C}_{22}\text{H}_{44}\text{O}_2$	3338.3	156.3×2	247.7

The following figures for bibasic acids are given :—

	Heat of combustion.	Heat of formation.
Malonic acid, $\text{C}_3\text{H}_4\text{O}_4$	207.3	212.7
Methylmalonic acid, $\text{C}_4\text{H}_6\text{O}_4$	362.5	220.5
Ethylmalonic acid, $\text{C}_5\text{H}_8\text{O}_4$	517.9	228.1
Dimethylmalonic acid, $\text{C}_6\text{H}_{10}\text{O}_4$..	515.3	230.7
Methylethylmalonic acid, $\text{C}_6\text{H}_{10}\text{O}_4$	676.0	233.0
Isopropylmalonic acid, $\text{C}_6\text{H}_{10}\text{O}_4$..	675.2	233.8
Propylmalonic acid, $\text{C}_7\text{H}_{12}\text{O}_4$	675.0	234.0
Diethylmalonic acid, $\text{C}_7\text{H}_{12}\text{O}_4$	832.9	239.1
Ethylpropylmalonic acid, $\text{C}_8\text{H}_{14}\text{O}_4$	989.9	245.0
Dipropylmalonic acid, $\text{C}_8\text{H}_{14}\text{O}_4$	1146.1	251.9
Heptylmalonic acid, $\text{C}_{10}\text{H}_{18}\text{O}_4$	1302.7	258.3
Octylmalonic acid, $\text{C}_{11}\text{H}_{20}\text{O}_4$	1458.5	265.5
Cetylmalonic acid, $\text{C}_{18}\text{H}_{36}\text{O}_4$	2707.7	320.3

The following conclusions concerning the formation of acids from the corresponding hydrocarbons, may be drawn :—(1) The reaction $-\text{H} + \text{COOH}$ is not represented by any constant thermal change. (2) The formation of solid monobasic saturated acids from the solid hydrocarbons is accompanied by a loss of energy represented by from 2.4 to 4.4 Cal. (3) In the transition of the monobasic saturated acids to the malonic acids, the thermal change is nearly nil. (4) In the

transition of acetic to malonic acid and of formic to oxalic acid, there is an increase of energy represented by 0.6 Cal. and 0.8 Cal. respectively.

(5) In the transition of solid monobasic acids to normal bibasic acids (except oxalic and malonic acids) there is a regular loss of energy, amounting to 5.1—8.3 Cal. in the groups with an even number of carbon atoms and to 3.3—5.4 Cal. in those with an uneven number of carbon atoms. (6) In the succinic series the transition of solid monobasic acids is accompanied by a regular loss of energy represented by 2.7—7.2 Cal.

The heat of combustion of allylmalonic acid, $C_5H_8O_4$, is 638.1 Cal.; that of benzylmalonic acid, $C_{10}H_{10}O_4$, is 1085.9 Cal.; that of tri-carballylic acid is 516.3 Cal.

A. G. B.

Cryoscopic Behaviour of Acetates of Feeble Bases. By A. GHIRA (*Gazzetta*, 23, ii, 598—601).—The acetates of triethylamine, diethylamine, piperidine, and coniine exercise abnormal depressions on the freezing point of benzene; their behaviour is thus analogous to that of the acetates previously examined by the author (*Abstr.*, 1893, i, 667).

W. J. P.

Solubility of Silver, Calcium, and Barium Ceanthylate, and of Calcium and Barium Trimethylacetate. By H. LANDAU (*Monatsh.*, 14, 707—718).—The solubilities were determined according to Raupenstrauch's method (*Monatsh.*, 1885, 563). Solubility curves are given in the original paper. The following equations were calculated from the results:—

Silver ceanthylate, $S = 0.063475 + 0.00188089t + 0.000001303t^2 + 0.00000006429t^3$.

Barium ceanthylate, from 1.6 to 30.7°, $S = 1.7602 + 0.00340552(t - 1.6) - 0.0000040143(t - 1.6)^2$; from 30.7 to 83.5°, $S = 1.6577 + 0.00609193(t - 30.7) + 0.000168803(t - 30.7)^2$.

Calcium ceanthylate from 2 to 15.8°, $S = 0.88986 - 0.0033093(t - 2) - 0.00031334(t - 2)^2$; from 15.8 to 41°, $S = 0.7849 - 0.00034732(t - 15.8) + 0.000017719(t - 15.8)^2$; from 41 to 76°, $S = 0.7874 + 0.004943(t - 41) - 0.00006826(t - 41)^2$.

Barium trimethylacetate, $S = 34.2546 - 0.0356536(t - 2) - 0.00251518(t - 2)^2 + 0.000047568(t - 2)^3$.

Calcium trimethylacetate, from 1 to 37.3°, $S = 7.2424 - 0.0517276(t - 1) + 0.00077773(t - 1)^2$; from 37.3 to 78.5°, $L = 6.3894 + 0.0177155(t - 37.3) + 0.00013074(t - 37.3)^2$.

E. C. R.

Parasorbic Acid. By O. DOEBNER (*Ber.*, 27, 344—351).—Parasorbic acid, $C_6H_8O_4$, was prepared by the author from the residue left after the extraction of malic acid from the juice of mountain ash berries. On distillation with steam and subsequent purification, it boiled at 221° under atmospheric pressure, and at 136° under 30 mm., a small quantity of resinous matter being always left behind. It did not solidify in a freezing mixture, and at 21° had the sp. gr. 1.0628. When pure it had no acid reaction, but became acid on standing. It

is dextrorotatory, having the specific rotation $[\alpha]_D = +40.8^\circ$, and its heat of combustion is 758.4 Cal.

It combines with bromine, yielding an oil of the composition $C_6H_5O_2Br_2$. No tetrabromide could be obtained.

Its salts do not correspond with an acid $C_6H_5O_2$, but with an acid $C_6H_5O_3$, the barium salt, for instance, being $Ba(C_6H_5O_3)_2$. The ethylic salt could not be prepared, ethylic sorbate being obtained in its stead.

Parasorbic acid passes into the isomeric sorbic acid when heated for a short time with solid potash and a few drops of water, the yield being 70 per cent. Sorbic acid on the other hand cannot be transformed into parasorbic acid.

These reactions point to the conclusion that whereas sorbic acid is a doubly unsaturated acid, $CH_3 \cdot CH : CH : CH : CH \cdot COOH$, the isomeric parasorbic acid is the lactone of a singly unsaturated acid, its formula being in all probability, $CH_3 \cdot CH : CH < \overset{CH}{\underset{O \cdot CO}{\curvearrowright}}} \cdot CH$.

J. W.

Crystalline Constituent of the Fruit of *Picramnia Cambolita* Engl. By B. GRÜTZNER (*Chem. Zeit.*, 17, 1851—1852).—The author has previously described an acid from the fat of the fruit of *picramnia cambolita* Engl.; further investigation has shown that the fat is a triglyceride of tariric acid, and is, therefore, identical with the fat obtained by Arnaud from the seeds of a shrub belonging to the genus *Picramnia* or *Tarari* (Abstr., 1892, 582). *Silver tarirate* crystallises in needles, darkens slowly on exposure to light, and commences to decompose at 160° . The *barium salt* is amorphous and anhydrous, and becomes yellow at 180° . The dibromo-additive compound melts at 32° . The tetrabromo-derivative, $C_{12}H_{12}Br_4O_2$, melts at 138° instead of 125° as stated by Arnaud (*loc. cit.*).

J. B. T.

Remarkable Intramolecular Change. By A. HANTZSCH (*Ber.*, 27, 355—356).—The author has repeatedly shown that the sole product in the direct bromination of ethylic acetoacetate is ethylic γ -bromoacetoacetate (compare this vol., i, 171), whilst, on the other hand, the bromination of ethylic cupracetoacetate leads to the exclusive formation of ethylic α -bromoacetoacetate. Experiments made with a sample of the α -derivative which had been prepared some months previously showed that it had undergone alteration, and further investigation proved that this compound, when allowed to remain at the ordinary temperature, is gradually converted into ethylic γ -bromoacetoacetate. As to the manner in which the change takes place nothing definite is known, but it may possibly be due to the intermediate formation of a trimethylene derivative, which then again reunites with the liberated hydrogen bromide, forming the γ -derivative. A somewhat similar intramolecular change has been observed by Wolff (Abstr., 1891, 416) who obtained glyoxylpropionic acid, $CHO \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$, by boiling dibromolevalinic acid, $CH_3 \cdot CO \cdot CBr_2 \cdot CH_2 \cdot COOH$, with water.

H. G. C.

Electrolysis of Salts of Organic Acids. By W. v. MILLER and J. HOFER (*Ber.*, 27, 461—470).—When a concentrated solution of sodium glycollate is electrolysed, no synthetic product is obtained, the acid undergoing oxidation to formaldehyde, carbonic anhydride, and carbonic oxide at the positive pole. Sodium α -hydroxybutyrate yields propaldehyde and a little formic acid as oxidation products, and the corresponding α -hydroxyisobutyrate yields acetone in addition. Potassium tartrate does not yield acetic acid and ethylene, as Bourgoin states, but formaldehyde and formic acid. Sodium β -hydroxybutyrate, when electrolysed, gives off unsaturated hydrocarbons at the positive pole. The salts of phenyl- β -lactic acid and mandelic acid yield benzaldehyde besides carbonic anhydride and carbonic oxide. The alkaline methoxyacetates give off the usual gases, the other oxidation products being formaldehyde, formic acid, methylal, and methylic alcohol. J. W.

Formula of the so-called Oxybrassicidic acid. By M. FILETI (*J. pr. Chem.*, [2], 49, 200).—The author corrects Baruch's quotation (*Abstr.*, 1893, i, 393) of his (the author's) statement that the formula in question is $C_{22}H_{45}O_3$, not $C_{22}H_{46}O_3$. A. G. B.

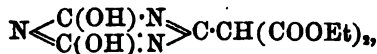
Hydration of the Calcium Salts of Succinic and Methyl-ethylacetic acids. By D. MILOJKOVIĆ (*Monatsh.*, 14, 699—706).—Calcium succinate, when crystallised at 20—22°, contains $3H_2O$. At 80—85° it crystallises with $1H_2O$. When the salt with $3H_2O$ is shaken with water at 60° it is converted into the salt with $1H_2O$, and the salt with $1H_2O$, when shaken with water at 23°, is converted into the salt with $3H_2O$. These results explain the bend which occurs at about 30° in the curve of solubility of calcium succinate. Calcium methylethylacetate, when crystallised at 23—26°, contains $3H_2O$; crystallised at 85—90°, it contains $1H_2O$. The two salts are convertible one into the other, in the same way as the calcium succinates of different degrees of hydration. When the salt with $3H_2O$ is shaken with water at 0° it is converted into a salt with $5H_2O$. These different degrees of hydration are shown on the solubility curve of the salt. E. C. R.

Action of Nitrous Acid on Ethylic Acetylglutarate. By G. BALDRACCO (*J. pr. Chem.*, [2], 49, 196—199).— γ -Isonitrosoacetobutyric acid, $COMe \cdot C(NO \cdot H) \cdot CH_2 \cdot CH_2 \cdot COOH$, is prepared by hydrolysing ethylic acetylglutarate with an alkali, adding sodium nitrite and acidifying; the new compound is dissolved out by shaking with ether. It crystallises from chloroform in large, transparent, colourless prisms (with $CHCl_3$), melts at 97—97.5°, and dissolves freely in alcohol, ether, and warm water, moderately in benzene and chloroform, but not at all in carbon bisulphide or light petroleum. Its alkaline solutions show the yellow colour characteristic of the $-CO \cdot C:NOH$ group. The barium salt, with $3H_2O$, and the hydrazone (m. p. 168°) are described. With hydroxylamine, it yields $\gamma\delta$ -isonitrosopropionic acid, $NOH \cdot CMe \cdot C(NO \cdot H) \cdot CH_2 \cdot CH_2 \cdot COOH$, which

crystallises in prisms, melts at 180.5° , and dissolves in water, alcohol, and ether; its solutions in alkalis are colourless. A. G. B.

Action of Ethylic Sodiomalonate on Cyanuric Chloride. By W. KOLB (*J. pr. Chem.*, [2], 49, 90—99).—In attempting to obtain a trisubstitution product from cyanuric chloride by its action on ethylic sodiomalonate, the author isolated a compound which crystallises in needles, melts at 190° and has a molecular weight corresponding with the formula $C_{24}N_3H_{23}O_{12}$.

Ethylic dihydrozycyanuromalonate,



was prepared by mixing cyanuric chloride with ethylic sodiomalonate in molecular proportion. It crystallises in white, lustrous needles, melts at 181° , and dissolves in alcohol and ether, but not in carbon bisulphide. The *silver* derivatives, $C_{10}N_3H_{10}Ag_3O_6$ and $C_{10}N_3H_{12}Ag_3O_6$, were obtained respectively by adding silver nitrate to an ammoniacal and to a neutral aqueous solution of the ethylic salt; the latter, when heated with methylic iodide, yields a *monomethylic* derivative as a white crystalline mass of ill-defined melting point. Attempts to separate the acid by hydrolysing the ethylic salt with potash failed. When strong hydrochloric acid at 130° is used as the hydrolys-

ing agent, *dihydrozycyanuracetic acid*, $N \begin{array}{c} \text{C(OH) \cdot N} \\ \text{C(OH) \cdot N} \end{array} > C \cdot CH_2 \cdot COOH$, is isolated; this crystallises in needles, decomposes at 180° without melting, and dissolves in water and dilute alcohol. The *silver* derivative, $C_6N_3H_3Ag_3O_6$, was prepared; when it is heated with methylic iodide in methyl alcohol, it is converted into *dihydrozycyanuromethane*, $C_3N_3(OH)_2Me$ (with 1 mol. H_2O), a crystalline mass, whose *silver* derivative, $C_4N_3H_3Ag_3O_6$, was prepared. A. G. B.

Rotatory Power of Tartrates. By P. PŘIBRAM (*Monatsh.*, 14, 739—745).—The author finds the following numbers for the rotatory power of the salts of tartaric acid in aqueous solution at 20° , P being the percentage strength of the solution; in each case corresponding with 0.2 gram of tartaric acid in 100 c.c. of water.

	P.	$[\alpha]_D$.	$[M]_D$.
$Li_2C_4H_4O_6$	0.216	35.58	57.63
$(NH_4)_2C_4H_4O_6$	0.245	35.46	65.24
$Na_2C_4H_4O_6$	0.2589	31.11	60.35
$K_2C_4H_4O_6$	0.3015	25.62	57.90
$Rb_2C_4H_4O_6$	0.4247	18.97	60.32
$Cs_2C_4H_4O_6$	0.5522	13.78	57.04
$Tl_2C_4H_4O_6$	0.7417	8.56	47.50
$NaHC_4H_4O_6$	0.2293	27.11	46.62
$KHC_4H_4O_6$	0.2505	21.57	40.17
$RbHC_4H_4O_6$	0.3116	18.38	43.00
$CsHC_4H_4O_6$	0.3754	15.84	44.67
$TlHC_4H_4O_6$	0.4692	12.07	42.57

It thus appears that Oudemann's law is obeyed by all the alkali tartrates with the exception of normal thallium tartrate (compare this vol. ii, 78). J. W.

Oxidation of Saccharic and Mucic acids with Potassium Permanganate. By E. FISCHER and A. W. CROSSLEY (*Ber.*, 27, 394—398).—It has long been known that saccharic acid on further oxidation with nitric acid yields tartaric acid, and that mucic acid under similar conditions is partly converted into racemic acid, but the results hitherto obtained have not been sufficiently definite to allow of conclusions being drawn as to the configuration of the two acids. The authors find that if a dilute solution of alkaline potassium permanganate is employed in place of nitric acid, much more satisfactory results are obtained, saccharic acid being thus converted into dextro-tartaric acid and an excess of oxalic acid, and mucic acid into racemic acid and oxalic acid. This reaction confirms the configuration of mucic acid deduced in the previous paper (this vol., i, 218), for the oxidation of an acid of this configuration might take place in two different ways, yielding in one case dextro- and in the other lævo-tartaric acid; and as the probability for both reactions is equal, the resulting compound is racemic acid.

With saccharic acid, the oxidation might also proceed in two different ways, leading to the formation of either dextro- or lævo-tartaric acid, but as a matter of fact only the dextro-acid is formed. Which of the two theoretically possible reactions actually occurs can only be decided when the exact relation of the configuration of dextrotartaric acid to glucose is known. The authors endeavoured to ascertain this by the oxidation of *d*-mannonic acid, which could only form one tartaric acid, but the yield obtained was so small that no definite conclusions could be drawn from it. H. G. C.

Conversion of Orthodiketo-chlorides into Chlorinated Keto-R-pentenes by Bleaching Powder. By T. ZINCKE (*Ber.*, 27, 562—564).—The orthodiketo-chlorides described in another paper (this vol., i, 234) are not converted by the usual reaction into chlorinated keto-R-pentenes of the $\gamma\gamma$ -series, compounds of the $\beta\gamma$ -series alone being formed. Compounds of both series are, however, formed at the same time, when the keto-chlorides are dissolved in methylic alcohol and treated with an aqueous solution of bleaching powder. The three following $\gamma\gamma$ -compounds have been thus prepared, $\text{CO} < \begin{smallmatrix} \text{CCl}_2 & \text{CCl} \\ | & | \\ \text{CCl}_2 & \text{CMe} \end{smallmatrix}$, $\text{CO} < \begin{smallmatrix} \text{CClMe} & \text{CCl} \\ | & | \\ \text{CCl}_2 & \text{CMe} \end{smallmatrix}$, whilst the $\beta\gamma$ -compounds $\text{CO} < \begin{smallmatrix} \text{CCl}_2 & \text{CMe} \\ | & | \\ \text{CClMe} & \text{CCl} \end{smallmatrix}$, $\text{CO} < \begin{smallmatrix} \text{CCl} & \text{CMe} \\ | & | \\ \text{CCl}_2 & \text{CCl}_2 \end{smallmatrix}$, have been obtained by the usual method. The $\gamma\gamma$ -ketones resemble the already known ketone, $\text{C}_5\text{Cl}_5\text{O}$, but do not react like it with ammonia. A. H.

Behaviour of Cinnamic Dichloride towards Micro-organisms. By A. STAVENHAGEN and H. FINKENBEINER (*Ber.*, 27, 456—457).—Cinnamic dichloride has been partially resolved into its optically

active components by Liebermann and Finkenbeiner (Abstr., 1893, i, 415). The authors have treated 5 grams of the dichloride for four weeks with *Aspergillus fumigatus*, and isolated 1.5 grams of an acid rotating $[\alpha]_D = +1$. From 6 grams of dichloride treated with yeast for three weeks, 2.2 grams of an acid was obtained, giving $[\alpha]_D = +2.8$. The organisms had multiplied during the above periods, despite the formation of hydrogen chloride and chlorocinnamene. Blank experiments (without the organisms) showed that whilst a small quantity of chlorocinnamene was formed, the acid remained inactive.

A. R. L.

Ketochlorides Derived from Phenol. By T. ZINCKE and C. SCHAUM (*Ber.*, 27, 537—559).—Tetrachloroketodihydrobenzene, $C_6Cl_4H_2O$, has been previously prepared by Benedikt (*Monatsh.*, 4, 233) from symmetrical trichlorophenol by the action of chlorine, but a better yield is obtained by the use of bleaching powder. The compound crystallises in almost colourless monosymmetric prisms, with a vitreous lustre, and melts at 122° (119° Benedikt). It is readily reconverted into trichlorophenol by the action of alkalis or acids. The position of the substituent groups is one of the following ($O : Cl_1 : Cl : Cl = 1 : 2 : 4 : 6$ or $1 : 4 : 2 : 6$).

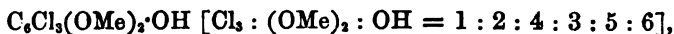
Hexachloroketodihydrobenzene, C_6Cl_6O , may be obtained from pentachloroaniline by the action of chlorine (Langer, *Annalen*, 215, 122) or from di- and tri-chloroaniline [$1 : 3 : 5$ and $1 : 3 : 4 : 5$. $NH_2 = 1$], but it is best prepared by heating α -heptachloroketotetrahydrobenzene (m. p. 98°) at 200 — 210° , the elements of hydrogen chloride being eliminated and the hexachloro-compound formed. The corresponding β -heptachloro-compound (m. p. 80°) yields the hexachloroketone when heated with an excess of potassium acetate and glacial acetic acid. Hexachloroketodihydrobenzene forms either tabular or needle-shaped crystals of the quadratic system. It melts at 106° and decomposes at 260° with formation of a substance of the formula $C_{12}Cl_8O_2$. It is converted into pentachlorophenol by reduction or by heating with 90 per cent. acetic acid; in acetic acid or chloroform solution, it is not altered by chlorine. It reacts with sodium methoxide, yielding the same substance as the heptachloroketones, from the nature of which its constitution has been deduced.

Heptachloroketotetrahydrobenzene, C_6Cl_7HO .—Two compounds of this formula are produced by the action of chlorine on metachloroaniline dissolved in acetic acid, the α -isomeride being formed in larger quantity. The substance melting at 78.5 — 80° , described by Beilstein (*Ber.*, 11, 2182) as formed by the chlorination of meta-chloroacetanilide, is probably a mixture of these. The α -compound crystallises in large, lustrous, monosymmetric prisms, which lose their lustre and transparency after a time. It is readily soluble in ether, chloroform, &c., less readily in light petroleum, and has a characteristic camphor-like odour. It melts at 98° , and decomposes at 170° , the hexachloroketone being formed. It is very readily reduced to tetrachlorophenol (Zincke and Wallbaum, Abstr., 1891, 708) by stannous chloride, sodium sulphite, or potassium iodide, and is converted into pentachlorophenol when boiled with potassium acetate and acetic acid or if heated with alcohol at 250° .

The β -compound forms lustrous, rhombic crystals, and behaves towards solvents in a similar manner to the α -compound. It melts at 80° , and when heated to 220° loses the elements of hydrogen chloride and chlorine, forming the compound $C_{12}Cl_6O_2$, which crystallises in soft, lustrous, white needles, does not melt below 280° , and is remarkably stable towards reagents. The β -heptachloro-ketone is reduced by stannous chloride to tetrachlorophenol, and by sodium sulphite and potassium iodide to pentachlorophenol, and when heated with potassium acetate, yields the hexachloroketo-compound, identical with that obtained by simply heating the isomeric α -heptachloro-ketone.

Action of Sodium Methoxide on Hexa- and Hepta-chloroketotetrahydrobenzene.—When one of these ketochlorides is dissolved in methylic alcohol and treated with sodium methoxide, the liquid being filtered from the common salt which separates, and then acidified, a substance of the formula $C_6Cl_3(OMe)_2OH$ is precipitated; this is sparingly soluble in ether, or light petroleum, but more readily in acetic acid, acetone, or methylic alcohol, from the last of which it separates in transparent, well-developed, tabular crystals, melting at 142 – 143° . It has a distinctly acid character, and forms a yellow, crystalline barium salt. When heated with aqueous soda or baryta water, it is converted into the compound $C_6Cl_3(OMe)_2(OH)O$, which is soluble in alkalis, whilst acids remove all the methoxy-groups, forming trichlorohydroxyquinone, $C_6Cl_3(OH)O_2$. When heated alone or in solution, the methylate loses a molecule of methylic alcohol, and forms the neutral compound $C_6Cl_3(OMe)_2O$, which is readily soluble in alcohol, &c., sparingly in light petroleum, crystallises in thick, transparent, yellow tablets, and melts at 78° . When a few drops of an aqueous alkali are added to its solution in methylic alcohol, it is reconverted into the tetramethoxy-derivative. It combines in the same manner with ethylic alcohol to form an *ethylate*, which forms small, white needles, melting at 140° with decomposition.

The compound $C_6Cl_3(OMe)_2O$, as well as its methylate, is converted by reduction into *trichlorodimethoxyphenol*,



which is readily soluble in alcohol, and crystallises in long, colourless needles melting at 110° . It dissolves without change in alkalis and alkali carbonates and yields an *acetate* which forms thick tablets and melts at 65° . Trichlorodimethoxyphenol is converted, by treatment with nitric acid, into *trichloroparamethoxyorthoquinone*, $C_6Cl_3(OMe)O_2$, which crystallises in deep red plates melting at 93 – 94° . It is reduced by aqueous sulphurous acid to *trichloroparamethoxycatechol*, $C_6Cl_3(OMe)(OH)_2$, which forms thick, pointed crystals melting at 118° . It is sparingly soluble in water, readily in alcohol and in aqueous alkalis, and is oxidised by nitric acid to the quinone. Its *acetate* crystallises in aggregates of short, thick needles melting at 103° .

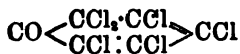
When the trichloromethoxyquinone is dissolved in acetic acid and concentrated hydrochloric acid is added, the red colour of the solution at first considerably deepens, and the liquid then probably contains

trichloroparahydroxyorthoquinone [$O : O : OH = 1 : 2 : 4$]; it soon becomes lighter in colour, however, and deposits the isomeric *trichlor-ortho-hydroxyparaquinone* [$O : OH : O = 1 : 2 : 4$], formed by intramolecular change; the latter is best prepared by boiling an acetic acid-solution of the methylate with hydrochloric acid. When the substance is slowly crystallised from ether, orange-red prisms are obtained, but, on heating, these are converted into a yellow powder, which melts at 194° ; this yellow powder is reconverted into the orange-red crystals by slow crystallisation from ether containing a little acetic acid. The quinone forms a deep-violet coloured solution in water, which is decolorised by mineral acids; its solution in aqueous soda is colourless, but becomes violet on dilution. When heated with an alkali, it is converted into chloranilic acid. On reduction, it is converted into *trichloroparahydroxyquinol*, $C_6Cl_3(OH)_2$, which melts at 160° and separates from benzene or acetic acid in crystals containing benzene or acetic acid of crystallisation. Its solution in water is colourless, but becomes violet when heated, whilst in alkalis it forms deep-green solutions, which become brown on standing, the quinone being formed. The *acetate* forms fine, white needles melting at 171° .

When the tetramethoxide, $C_6Cl_3(OMe)_4HO$, or the compound $C_6Cl_3(OMe)_3O$, is heated with dilute aqueous soda, it is converted into a substance of the formula $C_6Cl_3(OMe)_3(OH)O$, which forms thick, almost colourless needles melting at 159 – 160° . The *barium salt*, with $2H_2O$, crystallises in small, golden-yellow, lustrous tablets. The *acetate* forms colourless prisms melting at 91° . This substance is readily converted into trichlorohydroxyparaquinone by boiling with water or acids, but not in presence of alkalis.

Trichlororthomethoxyquinol, $OMe \cdot C_6Cl_3(OH)_2$, isomeric with the trichloromethoxycatechol, described above, is obtained from the foregoing compound by reduction with zinc dust in alkaline solution. It forms compact, colourless crystals melting at 116° . The *acetate* is readily formed, but has not been obtained in the crystalline state.

It follows from the nature of the reaction of the hexa- and heptachloroketones with sodium methoxide, that these compounds must be represented by the following formulæ.



Hexachloroketone.



Heptachloroketones.

Which of the two formulæ must be ascribed to the α - and which to the β -heptachloroketone has not yet been decided.

Octochloroketotetrahydrobenzene, which has been prepared by Benedikt (*Monatsh.*, 4, 607), from pentachlorophenol and by Zincke and Wallbaum from perchlorometahydroxybenzoic acid, cannot be prepared from the hexachloroketone and does not react with sodium methoxide in the cold. It has probably one of the following formulæ:



1 : 3 : 4 : 5-*Trichloraniline*, employed in the preparation of the hexachloroketone, is obtained from dichloroparanitraniline by means of the diazo-reaction and subsequent reduction. It forms long, brittle needles and melts at 100°. A. H.

Action of Chlorine on Ortho- and Para-Diamines. By T. ZINCKE (*Ber.*, 27, 560—562).—The chlorinated orthodiketones and orthoquinones have hitherto been prepared either directly from the quinones, or their reduction products, or by the action of chlorine on the hydrochlorides of the amidophenols. In addition to these methods, they may be readily obtained by the action of chlorine on the hydrochlorides of the orthodiamines dissolved in acetic acid. In this way, diketochlorides of toluene, trichlorotoluene, and metaxylene have been prepared, $\text{CMe} \langle \text{CCl}_2 \cdot \text{CCl}_2 \rangle \text{CO}$, $\text{CMe} \langle \text{CCl} \cdot \text{CCl}_2 \rangle \text{CCl}_2$, $\text{GCMe} \langle \text{CCl} \cdot \text{C}_2\text{Me} \rangle \text{CO}$, and these have been converted, by reduction and subsequent oxidation, into numerous derivatives. Similar derivatives have also been obtained from orthodiamidopseudocumene. These diketochlorides resemble hexachlorodiketone, $\text{C}_6\text{Cl}_6\text{O}_2$, in their general properties, but do not react in the usual manner with alkalis. The paradiamines may also be employed in a similar manner.

A. H.

Derivatives of Chloracetocatechol and Chlorogallacetophenone. By S. K. DZERZGOVSKY (*J. Russ. Chem. Soc.*, 25, 275—291).—*Dimethylamidoacetocatechol*, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NMe}_2$, is prepared by the action of dimethylamine (2 mols.) on chloracetocatechol (1 mol.) in alcoholic solution. The base itself can only be obtained with great difficulty. The oxalate, however, crystallises well from alcohol and from water, in colourless prisms which melt at 235° with partial decomposition. The hydrochloride can be obtained from the oxalate by precipitation with calcium chloride, and crystallises from water in needles melting at 232°.

Dimethylamidoacetopyrogallol, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NMe}_2$, can be prepared in like manner, chloracetopyrogallol being used instead of chloracetocatechol. The oxalate and tartrate crystallise in colourless prisms, melting at 190° and 205—206° respectively.

Anilidoacetocatechol, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NHPh}$, crystallises from alcohol in greenish-yellow prisms, melting at 149°. The corresponding orthotoluidide and paratoluidide melt at 157° and 103° respectively. *Methylanilidoacetocatechol* melts at 155°, and is sparingly soluble in boiling water.

Methylanilidoacetopyrogallol, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NMePh}$, crystallises in yellow plates, melting at 168°.

Dimethylaniline acts on the chloro-derivatives of acetopyrogallol and acetocatechol with formation of the *chlorides*



melting at 123° , and $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot NMe_2 \cdot PhCl$, melting at 162° with decomposition.

The following compounds have also been prepared by the author: *Paramidophenetolacetopyrogallol*, $C_6H_5(OH)_3 \cdot CO \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot OEt$, m. p. 144° . The *chlorides*, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot C_6NH_2Cl$, m. p. 139° , and $C_6H_5(OH)_3 \cdot CO \cdot CH_2 \cdot C_6NH_2Cl$, m. p. 104 from quinoline. The *chloride*, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot C_6NH_2Cl$, m. p. 265° with decomposition, from pyridine. The corresponding base, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot C_6NH_5 \cdot OH$, obtained from the sulphate and barium carbonate, melts at 188° . The *chloride*, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot C_6NH_2Cl$, m. p. 180° , from pyridine. *Piperidineacetocatechol*, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot C_6NH_{10}$, m. p. $187-188^{\circ}$. The chloride melts at 250° . J. W.

Thermochemical Values of the Functions of Orcinol. By DE FORCAND (*Compt. rend.*, 118, 284—286).—The sodium derivatives of orcinol alter rapidly when exposed to air, and also retain water or methylic alcohol even at moderately high temperatures. If ethylic alcohol is employed as the solvent, the results are not satisfactory. The monosodium derivative is best obtained by heating orcinol in a current of hydrogen with a solution of the calculated quantity of sodium hydroxide. The disodium derivative is prepared by dissolving anhydrous orcinol in absolute methylic alcohol, adding the calculated quantity of sodium, and afterwards expelling the methylic alcohol in a current of dry hydrogen. Both products are very deliquescent.

Heat of dissolution of anhydrous orcinol at $+10^{\circ} = -2.64$ Cal.; of the monosodium derivative, $+8.46$ Cal.; of the disodium derivative, $+17.44$ Cal. Berthelot and Werner's determinations of the heats of neutralisation were confirmed. It follows that

$C_7H_5(OH)_2$ sol. + Na sol. = H gas +	
$C_7H_5(OH)(ONa)$ sol.	develops $+40.23$ Cal.
$C_7H_5(OH)(ONa)$ sol. + Na sol. = H gas	
+ $C_7H_5(ONa)_2$ sol.	„ $+39.13$ „
$C_7H_5(OH)_2$ sol. + Na_2 sol. = H_2 gas +	
$C_7H_5(ONa)_2$ sol.	„ $+79.36$ „

The mean value of the two functions is $+39.68$ Cal., a number very similar to those obtained with other phenols. C. H. B.

Phloroglucitol. By W. WISLIZENUS (*Ber.*, 27, 357—359).—When phloroglucinol is carefully reduced by means of sodium amalgam in the cold in an approximately neutral solution, it is converted into 1:3:5-trihydroxyhexamethylene or *phloroglucitol*, $C_6H_{12}O_3$. This is extracted from the products of the reaction with ether, and the ethereal solution evaporated under diminished pressure. The syrup, after a time, deposits crystals of phloroglucitol, which can be purified by recrystallisation from water, or from dilute alcohol. It is thus obtained in well-developed colourless rhombohedra, which contain 2 mols. H_2O , the latter being gradually evolved in the desiccator, and completely

at 85°. When heated, it froths up at 115°, losing the water of crystallisation and again becoming solid, and on further heating the anhydrous compound melts at 184—185° and distils at about 300° almost without decomposition, if the quantity taken is small. It has a faint, purely sweet taste, and shows none of the colour reactions given by phloroglucinol.

H. G. C.

Carbamide Derivatives of Paraphenylenediamine. By H. SCHIFF and A. OSTROGOVICH (*Ber.*, 27, 398—401).—When tolidine dihydrochloride is treated with sodium acetate, the monhydrochloride is produced without any acetyltolidine, whereas the corresponding salt of paraphenylenediamine, when boiled with aqueous sodium acetate, is converted into *acetylparaphenylenediamine hydrochloride*, $\text{HCl} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$. When this substance is treated with a second molecule of sodium acetate, no diacetyl compound is produced, but the free base is simply separated. Acetylphenylenediamine reacts with ethylic chloroformate to form *acetamidophenylurethane*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{COOEt}$, which crystallises in small, hard prisms, melting at 202.5°. It dissolves in concentrated hydrochloric acid, and is converted, by boiling with this acid, into *amidophenylurethane hydrochloride*, which is readily soluble in water and alcohol, and melts, with decomposition, at 242—244°. The free base has been previously prepared by the reduction of the corresponding nitro-urethane. *Uramidophenylurethane*, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{COOEt}$, is obtained by the action of the hydrochloride on aqueous potassium cyanate. It is soluble in alcohol, insoluble in ether, and crystallises in colourless prisms, melting at 197—198°. *Di-acetylamidophenylcarbamide*, $\text{CO}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc})_2$, is prepared by fusing acetylphenylenediamine with carbamide; when the melt is extracted with dilute hydrochloric acid, it is left as a colourless, crystalline mass, which is almost insoluble in the usual solvents, and melts at 344° (corr.). The hydrochloric acid extract contains, in addition to unattacked acetylphenylenediamine, a small amount of *acetylamidophenylcarbamide*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$; this is more conveniently prepared by treating the hydrochloride of acetylphenylenediamine in aqueous solution with potassium cyanate, and evaporating over sulphuric acid. It forms long, thin prisms, melting at 354° (corr.). When it is boiled with hydrochloric acid, *paramidophenylcarbamide hydrochloride*, $\text{HCl} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, is produced; this crystallises in plates, is readily soluble in water, less readily in alcohol, and, when heated, decomposes without melting. The free base crystallises from ether in colourless plates, which become coloured on exposure to air, and melt at 129—130° (corr.).

The acid sulphate of *acetylamidophenylenediamine*, crystallises in small, colourless needles, which become coloured in the air, and melt at about 285°.

A. H.

Oxidation of Paraphenylenediamine. By E. BANDROWSKI (*Ber.*, 27, 480—486).—The product of this oxidation, by means of the oxygen of the air (*Abstr.*, 1889, 173), is now shown to have the

tripled formula $C_{18}H_{18}N_6$, probably $C_6H_5 < \begin{smallmatrix} N \cdot C_6H_5(NH_2)_2 \\ N \cdot C_6H_5(NH_2)_2 \end{smallmatrix} [N : (NH_2)_2] = 1 : 2 : 5$. It may be obtained crystallised with $1H_2O$ in bronze coloured crystals by oxidising an ammoniacal solution of the diamine by means of a current of oxygen, or with ammoniacal potassium ferricyanide. When reduced, best with ammonium sulphide, it yields a *leuco-product*, $C_{18}H_{20}N_6$, forming small, white crystals which oxidise readily in the air, and, when heated, cake at 160° , and melt and decompose at 230° . When more strongly reduced by heating with zinc-dust, it yields paraphenylenediamine. When heated with acetic anhydride, on the water bath or in a sealed tube, it yields a *tetracetyl derivative*, $C_{18}H_{14}Ac_4N_6$, which forms long, brick-red crystals, and crystallises from 75 per cent. alcohol with $2H_2O$ in red, quadratic crystals. When this derivative is heated with phenylhydrazine or ammonium sulphide in alcoholic solution, it is reduced to a *leuco-product*, $C_{18}H_{18}Ac_4N_6$, which forms woolly crystals turning red in the air, crystallises with $2HCl$ in white crystals, and, when heated with zinc and acetic acid, loses $2H_2O$, yielding an anhydride $C_{18}H_{14}N_6O_2$. This anhydride may be obtained directly from the acetyl derivative by reduction with zinc and 75 per cent. acetic acid; it crystallises in small quadratic or rhombic plates. C. F. B.

Diazo-compounds and Nitrosamines. By C. SCHRAUBE and C. SCHMIDT (*Ber.*, 27, 514—523).—*Sodium paranitrophenylnitrosamine* is obtained by adding a solution of paranitrodiazobenzene chloride to a solution of sodium hydroxide heated at 50 — 60° . The yield is quantitative. It crystallises from 90 per cent. alcohol with $1H_2O$, and, when heated at 50 — 60° , loses its water of crystallisation and turns bright yellow. The corresponding *potassium*, *barium*, and *calcium* salts are obtained in a similar way to the sodium salt. These salts do not explode when heated; at 180° they remain unaltered, and gradually blacken at 250° . The diazo-derivatives of ortho- and meta-nitraniline are also easily converted into nitrosamine salts, which are, however, so soluble that they have not been separated. *Paranitrophenylnitrosamine* is obtained as a bright yellow precipitate by acidifying an ice-cold solution of its salts with acetic acid. It is stable in ice-cold water, but when warmed decomposes with evolution of nitrogen. Sodium paranitrophenylnitrosamine is slowly converted into paranitrodiazobenzene chloride when allowed to remain with hydrochloric acid at 0° , and more rapidly at 20° ; a small quantity of the diazo-amido-compound is formed at the same time. Paranitromethylaniline is obtained when the above sodium salt is warmed with methylic iodide and methylic alcohol at 50 — 60° , and the nitroso-compound thus obtained is converted into the nitro-compound. The latter melts at 151° .

Potassium diazobenzene is obtained by adding diazobenzene chloride to a 67 per cent. solution of potassium hydroxide (100 parts), and warming the mixture on the water bath. The product cannot, however, be isolated, as it decomposes except in the presence of alkalis. If, however, a mixture of diazobenzene chloride and a 75 per cent. solution of potassium hydroxide is heated quickly at 130° and

finally at 140° , potassium phenylnitrosamine is obtained. It crystallises in silvery leaflets, and may be easily converted into monomethylaniline by heating with methylic iodide and methylic alcohol, and then eliminating the nitroso-group from the nitrosomethylaniline thus obtained.

E. C. R.

Benzenediazoic acid. By E. BAMBERGER (*Ber.*, **27**, 359—379; compare *Abstr.*, 1893, i, 327). In a previous paper, the author has shown that the benzenediazoic acid obtained by the oxidation of diazobenzene is, in all probability, either phenylnitramine, $\text{NPh}\cdot\text{NO}_2$, or phenylimidonitric acid, $\text{NPh}\cdot\text{NOOH}$, the former being the more probable. Further investigation has confirmed the first formula, but substances have also been obtained which appear to be derived from phenylimidonitric acid.

The acid is prepared in the manner already described, and with alkali metals yields salts, which crystallise in lustrous, white plates; it is decomposed by light with formation of ortho- and para-nitraniline, the latter in small quantity only. When carefully reduced with sodium amalgam in the cold, in a solution which is kept only slightly alkaline, it is converted into phenylhydrazine—aniline, ammonia, and other products being also formed. This reaction confirms the supposition that the constitution of the acid is represented by the formula $\text{NPh}\cdot\text{NO}_2$. In further confirmation of this formula, it is found that the sodium salt, on treatment with methylic iodide in alcoholic solution, yields the α -methyl derivative, $\text{NPhMe}\cdot\text{NO}_2$, which, on reduction, yields first phenylmethylnitrosamine,



and then asymmetrical methylphenylhydrazine, $\text{NMePh}\cdot\text{NH}_2$.

α -Methylic benzenediazoate crystallises in lustrous compact monosymmetric prisms or flat, satiny needles, melts at 38.5 — 39.5° , is almost odourless, volatilises in steam with very slight decomposition, and is unaffected by light. When boiled with 30 per cent. sulphuric acid, it undergoes an intramolecular change, forming *orthonitromethylaniline* and *paranitromethylaniline*. These compounds were also prepared for comparison by methylating ortho- and para-nitraniline; the former crystallises in orange-red needles having a violet shimmer, melting at 35 — 36° , and the latter in broad, yellow, lustrous prisms melting at 150 — 151° . On boiling with aqueous potash, the α -methylic salt is converted into ammonia, methylamine, aniline, and methylaniline.

If, instead of the sodium salt of benzenediazoic acid, the silver salt is treated with methylic iodide, an isomeric methylic salt is obtained, which may be termed the β -methylic salt; it has not yet been obtained pure, but differs very greatly from the α -derivative, having the usual properties of a diazo-compound. It is very unstable, has a pleasant heliotrope-like odour, and gives an immediate violet coloration with α -naphthylamine and acetic acid; when treated with mineral acids, it violently evolves gases consisting of nitrogen and its oxides, the residual solution containing aniline, methylaniline, ortho-nitraniline, paranitraniline, and small quantities of hydroxylamine and substances resembling nitrophenol.

An attempt was made to obtain a crystalline β -salt by acting on the silver salt with paranitrobenzyl chloride, but the reaction was so violent that the products were decomposed. The corresponding α -orthonitrobenzyl salt is readily prepared by the action of ortho-nitrobenzyl chloride on the sodium salt, and crystallises in broad, vitreous, colourless needles melting at 99.5° ; when dissolved in concentrated sulphuric acid, it undergoes the usual intramolecular change, with formation of *paranitrobenzylorthonitraniline*,



which forms golden-yellow, silky needles, and melts at 138° .

A further proof that the displaceable hydrogen atom in benzenediazoic acid is present as an imido-group is shown by the action of bleaching powder, which converts it into the *chlorimide*, $\text{NPhCl}\cdot\text{NO}_2$; this is a dark brown oil, which, when freshly prepared, has all the properties of the chlorimides, but, on remaining, even in the dark, for 24 hours undergoes intramolecular change with formation of 4:2-chloronitraniline, small quantities of the isomeric 2:4-chloronitraniline being also probably formed.

The formation of phenylnitramine, $\text{NHPh}\cdot\text{NO}_2$, by the oxidation of diazobenzene is a further confirmation of the supposition that this exists in two tautomeric forms, namely, $\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{OH}$ and $\text{NHPh}\cdot\text{NO}$; in the latter form it is the first representative of the series of aromatic nitrosamines.

H. G. G.

Nitration of Aniline. By E. BAMBERGER (*Ber.*, 27, 584—587; compare preceding abstract).—Benzenediazoic acid, $\text{NHPh}\cdot\text{NO}_2$, is obtained synthetically by the action of nitric anhydride on aniline in ethereal solution at -20° . The yield is 3.8 grams of crude acid from 10 grams of anhydride. In addition to benzenediazoic acid, aniline nitrate, diazobenzene nitrate, diazoamidobenzene, ortho- and para-nitraniline, and probably azobenzene are formed. The author gives full details of the methods employed for the separation and purification of these compounds, and of the tests by which they were identified. It has previously been shown how readily a nitro-group in the side chain "wanders" to the nucleus under the influence of mineral acids, and the author suggests that, in nitration, the hydrogen atom in the side chain is first replaced and that molecular rearrangement, caused by the excess of nitric acid, then takes place; in support of this, he refers to the ease with which hydrogen atoms in side chains react, and also to the formation of aromatic diazoamido- or amidoazo-derivatives according to the absence or presence of mineral acids.

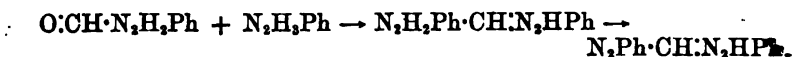
J. B. T.

Modes of Formation of Formazyl Compounds. By H. v. PECHMANN (*Ber.*, 27, 320—322).—These compounds can be prepared

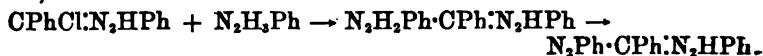
(1.) By the action of diazobenzene on phenylhydrazones, mostly in alkaline solution,



(2.) By the action of phenylhydrazine on phenylhydrazides, and spontaneous oxidation of the product, .



(3.) By the action of certain phenylhydrazones on phenylhydrazine,



This last method has only been observed in the one instance quoted.

Benzoylchloride phenylhydrazone, obtained by the action of phosphorus pentachloride on symmetrical benzoylphenylhydrazine, forms colourless crystals melting at 131° , and is converted into formazylbenzene when allowed to remain at the ordinary temperature with excess of phenylhydrazine in alcoholic solution. C. F. B.

Oxidation of Formazyl Compounds. By H. v. PRECHMANN and P. RUNGE (*Ber.*, 27, 323—324).—Oxidising agents cause formazylbenzene, $\text{NPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{N}\cdot\text{NPh}$, to take up an atom of oxygen, yielding a colourless ammonium base, probably $\text{CPh}\begin{matrix} \text{N}\cdot\text{NPh}\cdot\text{OH} \\ \text{N}\cdot\text{NPh} \end{matrix}$. The chloride and bromide of this base were analysed; they crystallise with 1 mol. of water, alcohol, or chloroform. From them, silver oxide liberates the base; this reacts strongly alkaline in aqueous solution, and is reconverted into formazylbenzene by reducing agents.

Formazyl-formic acid (hitherto called formazyl-carboxylic acid) and its ethylic salt yield analogous compounds. C. F. B.

Molecular Transformation of Oximes into Amides. By E. BECKMANN (*Ber.*, 27, 300—315).—The author inclines to the opinion that the agents which provoke this transformation act "catalytically," causing an interchange of position between atoms or groups of atoms in the molecule, and possibly a subsequent rearrangement of the atoms. In support of this view is the fact that molecular transformations are most frequently observed where a hydrogen atom or a hydroxyl group is concerned, these being just the two ions whose velocity of migration is the greatest. The agent used to induce the transformation serves to supply, from an external source, enough energy to bring about the movement of the atoms within the molecule. Something depends on the nature of this agent; just as, to draw an analogy, iodide of nitrogen is exploded only by sound waves of relatively great frequency. Conditions obtaining within the molecule also exert an influence; transformation being notoriously favoured by the greater relative proximity of the atoms or groups concerned, as, when they are in the "syn" position of Hantzsch, or in the "plane-symmetrical" position of Wislicenus.

For further details, reference must be made to the original paper, which it is impossible to abstract satisfactorily. C. F. B.

Synthesis of Oxanilide Dioxime. By A. F. HOLLEMANN (*Rec. Trav. Chim.*, 12, 290—297). The author has improved Wallach's

method (*Ber.*, 12, 1060; 13, 528) of preparing dithio-oxanilide, and confirms the melting point recorded by Wallach, namely, 133°. When dithio-oxanilide is heated on the water bath with an alcoholic solution of hydroxylamine (base), oxanilide dioxime is obtained; it appears to be identical with that prepared from dibromonitroacetonitrile (*Abstr.*, 1893, i, 494), but melts at 210° instead of 215°.

A. R. L.

Benzylthiocarbamides. By P. SPICA (*Gazzetta*, 23, ii, 553—558).—The author replies to Salkowski's criticism (this vol., i, 11) of Mazzaron's work (*Abstr.*, 1893, i, 411), and gives a short historical sketch of the subject.

W. J. P.

Ureides of α -Ketone Alcohols. By H. RUPE (*Ber.*, 27, 582—584).—By the action of potassium cyanate on amidoacetophenone hydrochloride in aqueous solution at 100°, a compound is obtained which crystallises from glacial acetic acid, or dilute hydrochloric acid, in silky, lustrous needles melting above 260°. It appears to be the ureide of acetophenone alcohol, being formed from the carbamide by elimination of 1 mol. H_2O , and has the formula $CO < \begin{smallmatrix} NH \cdot CPh \\ | \\ NH \cdot CH \end{smallmatrix}$ or

$CO < \begin{smallmatrix} N = CPh \\ | \\ NH \cdot CH \end{smallmatrix}$. The compound is soluble in dilute soda, and is re-precipitated on acidifying; in presence of alcohol, it gives a dark-brown coloration with ferric chloride, reduces alkaline copper and ammoniacal silver solutions immediately on heating, and the latter more slowly at ordinary temperatures. The *bromo-derivative* melts at 185° with decomposition. The *acetyl-derivative* crystallises in lustrous prisms melting at 157°. The *nitro-derivative* is deposited in slender needles; it melts at 160°, and, on treatment with soda, yields a compound crystallising in lustrous, flat needles melting at 213°. The relationship, if any, between the above compound and the one prepared by Marckwald and Ellinger from amidoacetal and carbamide (*Abstr.*, 1892, 1326), remains undetermined. Amidocamphor, hydrochloride, and potassium cyanate yield a *carbamide derivative* which crystallises in slender, colourless needles, and melts at 169°.

J. B. T.

Phosphazobenzene Chloride and its Derivatives. By A. MICHAELIS and G. SCHROETER (*Ber.*, 27, 490—497).—When aniline hydrochloride is heated with phosphorus trichloride, it yields *phosphazobenzene chloride*, $NPh \cdot PCl$ (analogous to diazobenzene chloride, $NPh \cdot NCl$, and thionylaniline, $NPh \cdot SO$). This forms transparent, white crystals, melts at 136—137°, and decomposes when distilled, even under reduced pressure. It is decomposed by various reagents, yielding aniline hydrochloride, and, with water, phosphorous acid, with alcohol, ethylic phosphite, with phenol, phenylic phosphite, with hydrogen chloride, phosphorus trichloride. It reacts with various other substances enumerated below, the chlorine atom being replaced; the products are decomposed by hydrochloric acid, yielding aniline hydrochloride, phosphorous acid, and some other compound. With

piperidine, it yields a *piperidide*, $\text{NPh}\cdot\text{P}\cdot\text{C}_6\text{NH}_5$, which crystallises in long, colourless needles, and melts, when heated quickly, at $202-203^\circ$. With aniline, it yields an *anilide*, $\text{NPh}\cdot\text{P}\cdot\text{NHPh}$ (analogous to diazoamidobenzene, $\text{NPh}\cdot\text{N}\cdot\text{NHPh}$, and phosphenylphenylhydrazone, $\text{PPh}\cdot\text{N}\cdot\text{NHPh}$), which forms a white, crystalline powder, melts at $152-153^\circ$, and from dilute alcohol crystallises in lustrous plates with H_2O (forming $\text{NPh}\cdot\text{P}\cdot\text{ONH}_2\text{Ph}$?). With sodium phenoxide, it yields a *phenylic ether*, $\text{NPh}\cdot\text{P}\cdot\text{OPh}$, which crystallises in small, lustrous prisms, and melts at $189-190^\circ$; with sodium ethoxide, an *ethylic ether*, $\text{NPh}\cdot\text{P}\cdot\text{OEt}$, as a thick oil; and with sodium benzoxide a *benzylic ether*, $\text{NPh}\cdot\text{P}\cdot\text{OCH}_2\text{Ph} + 2\text{H}_2\text{O}$, melting at 105° .

It has been already shown (this vol., i, 128) that with aniline hydrochloride, phosphoric oxychloride yields the compound $\text{NHPh}\cdot\text{POCl}_2$; it has since been shown that with excess of aniline hydrochloride it yields (NHPh), POCl_2 ; with free aniline, it yields (NHPh), PO . The three chlorine atoms of POCl_3 can thus be successively displaced by NHPh . This is not the case with phosphorus trichloride, from which, as above shown, only the compounds $\text{NPh}\cdot\text{PCl}_2$ and $\text{NPh}\cdot\text{P}\cdot\text{NHPh}$ are obtained. C. F. B.

A New Class of Non-nitrogenous Bases containing Iodine. By C. HARTMANN and V. MEYER (*Ber.*, 27, 426—432).—When iodosobenzene (5 grams) is dissolved in about 75 c.c. of concentrated sulphuric acid, kept cool, the solution assumes a dirty-brown colour, and does not contain iodosobenzene sulphate since it no longer liberates iodine from potassium iodide. The liquid is cautiously diluted with water at 0° , allowed to remain for two days, and then decanted from resinous deposits. It now contains the *sulphate* of a base, $\text{OH}\cdot\text{IPh}\cdot\text{C}_6\text{H}_4\text{I}$, being probably a derivative of the hypothetical base $\text{IH}_2\cdot\text{OH}$ (*iodonium hydroxide*), analogous to hydroxylamine. A similar change occurs with paraiodosotoluene. The *hydriodide*, $\text{C}_6\text{H}_4\text{I}_2$, separates on adding an alkali iodide to the solution of the sulphate just described, or better, to one of the base (see below) as a yellow, flocculent precipitate; it melts at 144° , decomposing into mono- and di-iodobenzene. The *hydrobromide* melts at $167-168^\circ$; the *hydrochloride* crystallises in white rosettes of needles, and melts at $200-201^\circ$ with decomposition. The *nitrate* is crystalline, melts at $158-161^\circ$, and dissolves sparingly in hot water, whilst the sulphate is amorphous and dissolves readily in water. The *chromate* is a brilliant yellow precipitate. The free base was not isolated, but a solution of it is best obtained when a solution of the hydriodide is shaken with moist silver oxide; it has a strong alkaline reaction, becomes turbid when kept, and, if evaporated, it is converted principally into an amorphous, gummy mass, together with a little para-di-iodobenzene. A. R. L.

Iodonium Bases. By C. HARTMANN and V. MEYER (*Ber.*, 27, 502—509).—*Diphenyliodonium iodide*, $\text{I}\cdot\text{IPh}$, is obtained by shaking equivalent quantities of iodosobenzene and iodobenzene with water and silver oxide during 3 to 4 hours. The filtrate, which contains the free base and its iodate, is reduced with sulphurous acid, and the

iodide precipitated with potassium iodide. The yield amounts to 98 per cent. of that required by theory. Lead oxide or potassium or sodium hydroxides may be substituted for the silver oxide, but the yield is then very small. The new base is also formed in small quantities in the preparation of iodobenzene, and in converting 35 grams of benzene iodic chloride into iodobenzene, 2.5 grams of the iodide, I_2Ph_3 , was obtained. The new iodide stands in the same relation to iodobenzene that trimethylsulphonium iodide does to methylic sulphide, and as tetramethylammonium iodide does to trimethylamine. It crystallises from alcohol in long, pale yellow needles, melts at $175-176^\circ$ with formation of iodobenzene (of which it is a polymeride), and turns dark yellow on exposure to light. When heated, it is decomposed into 2 mols. of iodobenzene, and if the decomposition is started at one point it proceeds through the whole mass with development of heat.

Diphenyliodonium hydroxide, $OH \cdot IPh_3$, is obtained by shaking the iodide with moist silver oxide. It has a strongly alkaline reaction in aqueous solution, is stable in dilute solutions, and may be evaporated to a syrup with only partial decomposition. The *chloride*, $C_{12}H_{10}ICl$, crystallises in flat, white needles, and decomposes at 230° into chlorobenzene and iodobenzene. The *bromide* crystallises in beautiful, white needles, and, like the chloride, decomposes at 230° . The *dichromate*, $(C_{12}H_{10}I)_2Cr_2O_7$, crystallises in beautiful, orange-red leaflets, and explodes when heated. The aqueous solution of the base readily absorbs carbonic anhydride; with potassium ferrocyanide, it gives an easily soluble precipitate crystallising in yellow needles, and with potassium ferricyanide a precipitate of sparingly soluble flat, yellow needles.

Diphenyliodonium hydroxide gives a precipitate with yellow ammonium sulphide, closely resembling freshly-precipitated antimony sulphide; with sodium sulphide, a bright yellow precipitate is obtained, which quickly decomposes into iodobenzene and phenylic sulphide.

The authors point out that iodine is an eminently base-forming element, that a compound constituted from hydroxyl and the negative radicles iodine and phenyl is an alkaline base, that phenyl, which does not form ammonium and sulphonium bases, forms iodonium bases; and that the new compounds closely resemble derivatives of certain heavy metals, especially thallium.

E. C. R.

Formation of Ethereal Salts of Aromatic Acids. By V. MEYER, H. GÜMBEL, and J. J. SUDBOROUGH (*Ber.*, 27, 510—512).—The authors have determined the amount of methylic salt formed when 0.5 gram of acid dissolved in 10 c.c. of methylic alcohol is treated with dry hydrogen chloride.

Benzoic acid, ortho-, meta-, and para-toluic acids, 1 : 3 : 5-dimethylbenzoic acid and unsymmetrical trimethylbenzoic acid (obtained by the oxidation of durene with nitric acid) yield from 83—95 per cent. of the theoretical quantity of ethereal salt, whilst the isomeric trimethylbenzoic acid (mesitylenecarboxylic acid) only yields from 8—9 per cent. Symmetrical tribromobenzoic acid $[COOH : Br, =$

1:2:4:6] yields about 2 per cent. of ethereal salt, whilst the isomeric tribromobenzoic acid [$\text{COOH} : \text{Br}_3 = 1:3:4:5$] yields 92–95 per cent. From these results, the authors conclude that those tri-substituted benzoic acids, which contain the substituents in the symmetrical position [1:3:5] are only converted into ethereal salts with difficulty, whereas their isomerides very easily yield ethereal salts.

The authors are engaged in the examination of the behaviour of the dibromo- and tetrabromo-acids under similar conditions. E. C. R.

Preparation of Symmetrical and Unsymmetrical Tribromobenzoic acids. By J. J. SUDBOROUGH (*Ber.*, 27, 512–514). The acids, which are somewhat difficult to prepare, may be obtained by the following methods.

Symmetrical tribromobenzoic acid, [$\text{COOH} : \text{Br}_3 = 1:2:4:6$], is obtained by diazotising tribromaniline, and gradually adding the solution to a solution of cuprous potassium cyanide heated at 90° . The nitrile thus obtained is extracted with ether, and heated with concentrated hydrochloric acid at $200\text{--}230^\circ$ for 6–7 hours. The acid crystallises in small, white needles, and melts at 187° .

Unsymmetrical tribromobenzoic acid, [$\text{COOH} : \text{Br}_3 = 1:3:4:5$], is obtained as follows:—2:5:4-dibromamidobenzoic acid, dissolved in dilute soda, is treated with sodium nitrite, and the mixture gradually poured into concentrated sulphuric acid, cooled with pieces of ice. The diazotised mixture is then gradually added to a boiling solution of cuprous bromide. The acid crystallises in beautiful needles, and melts at 235° . The *methylic salt* crystallises in needles, and melts at 154° . E. C. R.

Formation of Chlorobenzoic and Bromobenzoic Anhydrides By G. D. MOORE and D. F. O'REGAN (*Chem. Centr.*, 1893, ii, 938; from *Proc. Amer. Acad.*, 1893, 222–225). Working on similar lines to those by which they have already obtained anhydrides of nitrobenzoic acids the authors have obtained anhydrides by the action of phosphoric anhydride on halogen substituted benzoic acids dissolved in boiling benzene. *Orthochlorobenzoic anhydride* is easily soluble in alcohol, ether, chloroform, and benzene, sparingly in light petroleum, and crystallises in glistening, white needles. *Metachlorobenzoic anhydride* resembles the ortho-compound in solubility, and crystallises from benzene in yellowish-white needles. The *para-derivative* resembles the other two, and melts at 186° . *Orthobromobenzoic anhydride* crystallises in white, prismatic needles melting at 141° ; the *metabromo-derivative* yields similar needles melting at 97° , and the *para* compound melts at $212\text{--}213^\circ$. L. T. T.

Isomeric Octonaphthenic (Cyclohexamethylcarboxylic or Hexahydrorthotoluic) acids. By V. MARKOVNIKOFF (*J. pr. Chem.*, [2], 49, 64–89).—*Orthoctonaphthenic acid*, $\text{C}_8\text{H}_{10}\text{MeCOOH}$ [= 1:2], is prepared from orthotoluic acid (b. p. $258\cdot5\text{--}259^\circ$ at 751 mm.; m. p. 102°) by a method differing only in detail from that prescribed

for the preparation of heptanaphthenic acid (Abstr., 1893, i, 93). It crystallises in needles, melts at 50—52°, boils at 241—242° (746 mm.), and dissolves sparingly in cold water, more freely in hot water, ether, chloroform, alcohol, light petroleum, and hot benzene. It is more volatile with steam than is hexanaphthenic acid. The *sodium*, *silver*, *calcium* (with $1\frac{1}{2}\text{H}_2\text{O}$), *barium*, and *zinc* salts are described; the three last are much less soluble in hot than in cold water. The *methylic* salt boils at 190° (769 mm.), and has a sp. gr. of 0.9929 at 0°/0°. Unlike the amides of most of the naphthenic acids, the *amide* of that under consideration cannot be obtained by heating the methylic salt with aqueous ammonia, but is prepared by heating the acid with phosphoric chloride in light petroleum, and passing ammonia through the solution; it crystallises in flat, lustrous needles, melts at 180—181°, and dissolves sparingly in water. Orthomethylnaphthenic acid is not altered when heated with anhydrous copper sulphate.

Metaoctonaphthenic acid, (Me : COOH = 1 : 3), from metatoluic acid, is a viscid, colourless liquid, which does not solidify at -15°; it boils at 245°, is slightly volatile with steam, and dissolves easily in most solvents except water. Its sp. gr. is 1.01822 at 0°/0°. The *sodium* salt is amorphous; the *calcium* salt, with $4\text{H}_2\text{O}$, is crystalline and more soluble in hot than in cold water; the *barium* and *zinc* salts are crystalline and less soluble in hot than in cold water; the *silver* salt is a pulverulent precipitate; the *methylic* salt boils at 196—197°, and has a sp. gr. of 0.97297 at 0°/0°; when heated with aqueous ammonia, it yields the *amide* which melts at 155—156°.

Paraoctonaphthenic acid, [Me : COOH = 1 : 4], from paratoluic acid, is a crystalline substance; it melts at 110—111°, boils at 245° with partial decomposition, sublimes in laminae at 100°, and dissolves freely in alcohol, ether, chloroform, and light petroleum, but only sparingly in water. The *sodium*, *calcium*, *barium*, *silver*, and *zinc* salts are described; the last-named is more soluble in cold than in hot water. The *methylic* salt boils at 192—194° (748 mm.), and has a sp. gr. of 0.9687 at 0°/0°; when heated with aqueous ammonia, it yields the *amide*, which melts at 220—221°.

α-Octonaphthenic acid has not been obtained from phenylacetic acid; it constitutes the main portion of the acid separated from naphtha, and its isolation is fully detailed, the principle of the operations being the fractional saturation of the acids with alkali, and the distillation of the free acid in steam. It is an oily liquid which does not solidify at -20°; it boils at 237—238° (750 mm.), has a sp. gr. of 1.0020 at 0°/0°, and is sparingly soluble in cold water. The *sodium*, *silver*, *calcium*, and *zinc* salts are described; the two last are more soluble in cold than in hot water. The *methylic* salt boils at 189—190° (corr.), and the *amide* melts at 128—129°. The constitution of the acid is discussed by the light of the fact that when heated with hydriodic acid it yields an octonaphthene, which is convertible into tetrabromoparaxylene; the most probable conclusion is that the acid is a stereoisomeride of metaoctonaphthenic acid; but the attachment of both CH_3 and COOH to the same carbon atom is not wholly improbable. An investigation of the lower boiling methylic salts obtained

from natural naphthenic acid is described, but no definite conclusions are stated.

A. G. B.

Reduction of Salicylic acid. By A. EINHORN and R. WILLS-TÄTTER (*Ber.*, 27, 331).—In a previous paper (this vol., i, 87), the authors stated that one of the products of the reduction of salicylic acid by sodium in amyl alcohol solution was hexahydrosalicylic acid. They now find that the substance melting at 105° is not, as they supposed, hexahydrosalicylic acid, but normal pimelic acid.

J. W.

An Isomeride of Fraxetin and its Derivatives. By P. BIGINELLI (*Gazzetta*, 23, ii, 608—620).—*Hydroxydimethoxy-β-methylcoumarin*,

$\text{OH} \cdot \text{C}_6\text{H}(\text{OMe})_2 \cdot \text{C} \begin{smallmatrix} \text{Me}:\text{CH} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$, is prepared by the action of concentrated

sulphuric acid on a hot solution of dimethoxyquinol in ethylic acetate, or by reducing the solution with stannic chloride; the former process gives an almost theoretical yield, whilst the latter gives a somewhat smaller one. The coumarin forms tabular, colourless crystals melting at 191—191·5°; it is soluble in potash, the solution sometimes showing a bluish-green fluorescence. On boiling with alcoholic potash and methylic iodide, it yields *trimethoxy-β-methylcoumarin potassium iodide*, $(\text{C}_{13}\text{H}_{14}\text{O}_4)_2\text{KI}$, which separates from absolute alcohol in small, yellowish, monosymmetric prisms, $a : b : c = 0\cdot5942 : 1 : 0\cdot3658$; $\beta = 85^\circ 48'$, and decomposes at 220°. *Trimethoxy-β-methylcoumarin* is obtained on treating this double compound with hot water; it forms long, monosymmetric needles, $a : b : c = 0\cdot9187 : 1 : 1\cdot2551$; $\beta = 84\cdot19^\circ$, melts at 116—117°, is very soluble in alcohol, and is found to contain three methoxy-groups by Zeisel's method.

Trihydroxy-β-methylcoumarin, $\text{C}_6\text{H}(\text{OH})_3 \cdot \text{C} \begin{smallmatrix} \text{Me}:\text{CH} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$, is prepared by heating the preceding substance with hydriodic acid, methylic iodide being simultaneously formed; it crystallises in minute scales, melts at 244—246°, and yields the above methoxy-derivative on methylation. If excess of concentrated hydriodic acid is used in its preparation, a substance, $\text{C}_{13}\text{H}_{14}\text{O}_6$, is obtained, which forms white, anorthic scales melting at 253—254°; $a : b : c = 0\cdot483 : 1 : 0\cdot622$; $\alpha = 95^\circ 13'$; $\beta = 107^\circ 14'$; $\gamma = 101^\circ 41'$. The author assigns to this the following constitution:— $\text{C}_6\text{H}(\text{OH})_3 \cdot \text{C} \begin{smallmatrix} \text{Me}:\text{CH} \\ \text{O} \text{---} \text{CO} \end{smallmatrix} \cdot \text{C} \begin{smallmatrix} \text{Me}:\text{CH} \\ \text{O} \text{---} \text{CO} \end{smallmatrix} \cdot \text{C}_6\text{H}(\text{OH})_3$.

On heating trimethoxy-β-methylcoumarin with excess of alcoholic potash and methylic iodide under given conditions, the methylic salts of two tetramethoxy-β-methylcinnamic acids,



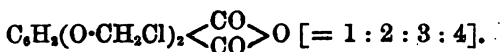
are obtained. The methylic salt which is least soluble in light petroleum, forms lustrous, monosymmetric prisms; $a : b : c = 0\cdot6045 : 1 : 0\cdot4590$; $\beta = 56^\circ 29'$; it melts at 77·5—78°. The corresponding acid is obtained in monosymmetric prisms; $a : b : c = 1\cdot7223 : 1 : 2\cdot3075$; $\beta = 57^\circ 23'$; this melts at 148—149°, and

when dissolved in alkali carbonates, and reprecipitated with hydrochloric acid it is partially converted into the isomeric acid described below.

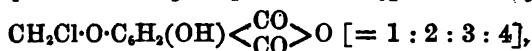
The second methylic salt crystallises in needles melting at 67—68°; the acid from which it is derived forms anorthic crystals; $a : b : c = 0.7217 : 1 : 0.8834$; $\alpha = 100^\circ 37'$; $\beta = 101^\circ 29'$; $\gamma = 61^\circ 15'$. It may be partially converted into the isomeric acid by heat or by treatment with mineral acids. The author is still engaged with the investigation of these acids.

W. J. P.

Norhemipinic acid. By M. FREUND and F. HORST (*Ber.*, 27, 332—339).—Hemipinic acid (1 mol.), when heated with phosphorus pentachloride (5 mols.) for five hours at 170—175°, gives a yellow liquid, which decomposes when poured into water, yielding an oil which crystallises after a time. The crystals, when washed with ether and recrystallised from benzene, are colourless and melt at 166°. The substance is *orthodichloromethoxyphthalic anhydride*,



On boiling with water, it yields formaldehyde, hydrogen chloride, and norhemipinic acid. A crystalline product obtained in another experiment proved to be *hydroxychloromethoxyphthalic anhydride*,



melting at 130—135°.

Norhemipinic acid, $\text{C}_{10}\text{H}_{10}\text{O}_6 + \text{H}_2\text{O}$, is obtained directly from the product of the interaction of hemipinic acid and phosphorus pentachloride by pouring it into water and digesting for several hours on the water bath. The filtered solution is then boiled for some time, treated with animal charcoal, and evaporated to crystallisation. The acid is purified by again boiling with animal charcoal, and precipitating with concentrated hydrochloric acid. To obtain it in the perfectly pure condition, it must be prepared from the pure ammonium or barium salt. It crystallises from water in long, narrow, colourless, rhombic plates or in thick, rhombic prisms, containing $1\text{H}_2\text{O}$, which is lost at 105°, leaving the anhydrous acid, this melts at 210—212°, decomposing into the anhydride and water. It dissolves easily in alcohol and in hot water, and is almost insoluble in ether, benzene, and light petroleum.

The *ammonium* salt is anhydrous and melts at 202° with decomposition. Its solutions give precipitates with silver, barium, calcium, cupric, ferric, and lead salts. On careful addition of acid, the *ammonium hydrogen* salt, $\text{C}_6\text{H}_2\text{O}_4\text{NH}_4 + \text{H}_2\text{O}$, may be precipitated. The *barium* salt, with $2\text{H}_2\text{O}$, and *calcium* salt, with $3\text{H}_2\text{O}$, are described.

When the anhydrous acid is heated for one hour at 205—210°, it changes into a brownish mass, which, when dissolved in alcohol and precipitated with water, yields the *anhydride*, $\text{C}_6\text{H}_2\text{O}_6 + 2\text{H}_2\text{O}$, melting at 238°. The anhydride is soluble in much hot water, giving a solution with a splendid green fluorescence; it is insoluble in

benzene. No fluoresceïn is obtained on heating it with resorcinol. It is strongly acid, and gives a barium salt, $(C_6H_5O_3)_2Ba + 4H_2O$.
J. W.

Mercury Derivatives from Dimethylaniline. By L. PESCI (*Gazzetta*, 23, ii, 521—529; compare Abstr., 1893, i, 24).—Yellow mercuric oxide dissolves readily in an aqueous solution of dimethylaniline acetate, and separation of *paramercurodiphenylenetetramethylmercuriodiammonium acetate*, $Hg<\overset{C_6H_5 \cdot NMe_2(OAc)}{C_6H_5 \cdot NMe_2(OAc)}>Hg$, occurs; it is obtained in thin needles melting at 162° ; is soluble in benzene, chloroform, acetic acid or boiling alcohol, but insoluble in water. It yields the *hydroxide* on treatment with caustic potash; this crystallises in microscopic prisms, melts at 179° , and is very sparingly soluble in cold water, giving a feebly alkaline solution. The *chloride* separates from boiling alcohol in lustrous, colourless laminæ; it is soluble in boiling benzene but not in water, and is changed by light.

On boiling the hydroxide described above with methylic iodide, *paramercurodimethylaniline methiodide*, $Hg(C_6H_5 \cdot NMe_2I)_2$, is obtained; it crystallises from boiling water in very thin, flexible needles melting at about 230° . It is not attacked by boiling potash, and is soluble in boiling alcohol. On treatment with silver oxide, it yields *paramercurodiphenylenehexamethylidiammonium hydroxide*, $Hg(C_6H_5 \cdot NMe_2OH)_2$, as a caustic liquid, which rapidly absorbs carbonic anhydride. The *chloride* crystallises in small, thin needles, and is soluble in water and in alcohol; with mercuric chloride, it yields a double salt, which crystallises in laminæ and melts at 225° with decomposition.

Paramercurodimethylaniline methiodide yields trimethylphenylammonium iodide on reduction with sodium sulphide; the hydroxide, on similar treatment, gives paramercurodimethylaniline. The latter, when heated with methylic iodide, yields paramercurodimethylaniline methiodide. On treating an alcoholic solution of paramercurodiphenylenehexamethylammonium chloride with bromine, parabromotrimethylphenylammonium chloride is obtained. These reactions prove the constitution of the compounds described above.

W. J. P.

Constitution of Mercurophenylamine and of Methylphenylmercurammonium Hydroxide. By L. PESCI (*Gazzetta*, 23, ii, 529—533).—The base, which the author has previously described as mercurophenylamine (Abstr., 1892, 1448), yields paramercurodimethylaniline methiodide on boiling with methylic alcohol and methylic iodide; mercurophenylamine, therefore, has the constitution $Hg<\overset{C_6H_5 \cdot NH}{C_6H_5 \cdot NH}>Hg$, and the name must, consequently be changed to paramercurodiphenylenemercurodiamine.

Methylphenylmercurammonium hydroxide, on treatment with methylic iodide, yields a crystalline product, which gives paramercurodimethylaniline methiodide and mercuric sulphide on the addition of barium sulphide. The hydroxide, therefore, has the constitution

$\text{Hg} < \begin{smallmatrix} \text{C}_6\text{H}_4\cdot\text{NHMe}(\text{OH}) \\ \text{C}_6\text{H}_4\cdot\text{NHMe}(\text{OH}) \end{smallmatrix} > \text{Hg}$, and should be termed *paramercurodiphenylenedimethylmercurodiammonium hydroxide*.

Paramercuroaniline, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, is prepared by heating paramercurodiphenylenemercurodiamine with sodium sulphide on the water bath; it is extracted from the product by chloroform, and is ultimately obtained in yellowish needles melting at 174° with decomposition.

Paramercuromethylaniline, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NHMe})_2$, is obtained by the action of sodium sulphide on paramercurodiphenylenedimethylmercurodiammonium hydroxide; it separates from its benzene solution in lustrous, colourless needles melting at $178\text{--}179^\circ$, and is sparingly soluble in alcohol. W. J. P.

Mercury Derivatives from Diethylaniline. By A. PICCININI (*Gazzetta*, 23, ii, 534—543).—The author has prepared a number of aromatic mercury-derivatives from diethylaniline analogous to those obtained by Pesci (see preceding Abstract) from dimethylaniline.

Paramercurodiphenylenetetrethylmercurodiammonium acetate,



crystallises in long, colourless needles melting at $104\cdot4^\circ$. The *hydroxide* is obtained in colourless needles melting at 200° with decomposition; it has a strongly alkaline reaction, and is slowly decomposed by boiling water. The *chloride* forms thin, colourless needles melting at $164\cdot5^\circ$, and is sparingly soluble in hot water.

Paramercurodiethylaniline methiodide, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NEt}_2\text{MeI})_2$, crystallises in colourless prisms, melting at $202\cdot8^\circ$ with decomposition, and is very soluble in boiling water; the *methoxide* was only obtained in aqueous solution. The *methochloride* crystallises in thin, colourless, deliquescent needles, and forms a double salt with mercuric chloride, which separates from boiling water in lustrous laminæ, melting at about 200° with decomposition.

On reducing the preceding methiodide with sodium sulphide, a salt of diethylmethylphenylammonium is obtained.

On reducing parabromodiethylaniline with sodium amalgam, *mercuriodiethylaniline*, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NEt}_2)_2$, is produced; it crystallises from benzene in colourless, efflorescent prisms, melting at $160\cdot6^\circ$. The constitution of paramercurodiethylaniline methoxide is proved by the fact that it yields the same mercuriodiethylaniline on reduction with sodium sulphide. W. J. P.

Mercury Derivatives from Ethylaniline. By G. RUSPAGGIARI (*Gazzetta*, 23, ii, 544—548; compare preceding Abstracts).—*Paramercurodiphenylenediethyldiammonium acetate*,



separates from a solution of mercuric acetate in an alcoholic solution of ethylaniline; it crystallises in colourless, transparent prisms, VOL. LXVI. i.

and melts at 130°. It is insoluble in cold water, and is decomposed by hot water. On treatment with potash, it yields the *hydroxide*, which crystallises in beautiful, colourless needles, decomposing at 145°; this is soluble in hot water, giving a strongly alkaline solution. The *chloride* separates from alcohol in lustrous, six-sided laminæ, melting at 142°, and is decomposed by boiling water. On heating the base with methylic alcohol and methylic iodide in a reflux apparatus, it yields *paramercurodiphenylenetetramethyldiethyldiammonium iodide*, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NEtMe}_2\text{I})_2$, which crystallises in long, colourless needles melting at 202°. On treating its aqueous solution with silver chloride, the corresponding *chloride* is obtained in long, colourless needles, very soluble in water. With mercuric chloride, it forms a double *compound*, which melts at 169°.

Mercurioethylaniline, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NHet})_2$, is obtained by reducing paramercurodiphenylenediethylmercurodiammonium hydroxide with sodium sulphide. It crystallises in lustrous laminæ, melting at 166°. W. J. P.

Derivatives of Disulphobenzoic acid [1:3:5]. By K. HOFFGARTNER (*Monatsh.*, 14, 685—698).—*Disulphobenzoic trichloride*,



is obtained by heating dry potassium disulphobenzoate, $\text{C}_7\text{H}_3\text{O}_6\text{S}_2\text{K}_2$, with phosphoric chloride in an oil bath at 150°. A better yield is obtained by heating the mixture in sealed tubes in a bath of amylic alcohol. From benzene, it crystallises with 1 molecule of the solvent in large, colourless prisms. When free from benzene, it melts at 86.5—87° (uncorr.). The *salt*, $\text{C}_7\text{H}_3\text{O}_6\text{S}_2\text{K}_2 + 3\text{H}_2\text{O}$, is obtained from the crude melt, after the trichloride has been extracted with benzene, by crystallising the residue from water; it forms yellowish, flat prisms.

Disulphobenzoic dichloride, $\text{C}_7\text{H}_3\text{O}_6\text{S}_2\text{Cl}_2$, is obtained by allowing the trichloride to remain with water for some time at the ordinary temperature. It is a white, crystalline powder, softens at 180°, melts at 183° (uncorr.), and is easily dissolved in dilute soda solution, and by shaking with barium carbonate and water.

The *amide*, $\text{C}_7\text{H}_3\text{O}_6\text{S}_2\text{N}_2$, obtained by treating with dry ammonia the trichloride dissolved in benzene, crystallises in long, thin, lustrous, white needles, begins to give off ammonia at 230°, and melts at 290°. The *trianilide*, $\text{C}_{22}\text{H}_{11}\text{O}_6\text{S}_2\text{N}_3$, obtained by treating the trichloride with aniline, is a white, crystalline powder, and melts at 222° (uncorr.).

Sulphohydroxybenzoic acid, $\text{C}_7\text{H}_3\text{O}_6\text{S}$, is obtained by warming the tripotassium disulphobenzoate with a solution of potassium hydroxide at 160—165°, and is purified by means of the lead salt. It forms white crusts of microscopic needles, containing $1\text{H}_2\text{O}$, begins to decompose at 100°, but does not melt at 180°, is very hygroscopic, has a strongly acid reaction, and gives a faint reddish-brown coloration with ferric chloride. The *lead salt*, $\text{C}_7\text{H}_3\text{SO}_6\text{Pb} + 3\frac{1}{2}\text{H}_2\text{O}$, crystallises in slender, white, lustrous needles, and decomposes before it

melts. The *potassium* salt, with $3\text{H}_2\text{O}$, crystallises in small, colourless prisms.

Dihydroxybenzoic acid [1 : 3 : 5] is obtained by heating the potassium salt of disulphobenzoic acid with potassium hydroxide at $250\text{--}260^\circ$.
E. C. R.

Formation of Substituted Benzophenones. By G. D. MOORE and D. F. O'REGAN (*Chem. Centr.*, 1893, ii, 988; from *Proc. Amer. Acad.*, 1893, 226—233).—Kollarits and Merz showed (this Journal, 1872, 707; and 1873, 1035) that by heating benzoic acid or anhydride with benzene and phosphoric anhydride, benzophenone is formed. Employing this reaction with their substituted benzoic anhydrides (this vol., i, 244) the authors obtained orthonitrobenzophenone, *meta*-nitrobenzophenone, melting at $94\text{--}95^\circ$, *para*-nitrobenzophenone, melting at $137\text{--}138^\circ$, and ortho-, meta-, and para-chloro-, and meta- and para-bromo-benzophenones.
L. T. T.

Isostilbene. By V. REDZKO (*J. Russ. Chem. Soc.*, 25, 297—298).—When isostilbene, CPh_2CH_2 , is treated with fuming hydriodic acid at the ordinary temperature, a solid, crystalline substance is formed, which melts at 143° , has the empirical formula C_7H_8 , and is in all probability a polymeride of isostilbene. Gaseous hydrogen iodide, as well as strong sulphuric acid, also produces it at the ordinary temperature. If the fuming hydriodic acid is made to act slowly on isostilbene at the temperature of a good freezing mixture, diphenylethane (b. p. $272.5\text{--}273^\circ$) is formed, along with small quantities of the solid melting at 143° .

When bromine and isostilbene, both dissolved in light petroleum, are allowed to react in a freezing mixture, the bromide, $\text{CPh}_2\text{BrCH}_2\text{Br}$, is obtained in colourless prisms, which may be dissolved in boiling light petroleum without decomposition. At its melting point, about 65° , the dibromide decomposes with evolution of hydrogen bromide. Even at the ordinary temperature, hydrogen bromide is given off slowly, the dibromide first melting and a solid being afterwards formed, which, from its melting point and crystalline form, was proved to be diphenylbromomethylene, CPh_2CHBr .

Alcohol acts on the dibromide at the ordinary temperature with formation of a crystalline compound melting at $98\text{--}99^\circ$. This substance is an ethoxybromodiphenylethane, the ethoxyl group being probably attached to the carbon atom which is united to the two phenyl groups.
J. W.

Derivatives of Naphthyl Ethyl Ether. By P. HEERMANN (*J. pr. Chem.*, [2], 49, 130—134).—1 : 4-Ethoxynaphthalenesulphonic acid, $\text{OEt}\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$, is very easily formed by sulphonating α -naphthyl ethyl ether with strong sulphuric acid. It is soluble in water, as is also its sodium salt, which, however, is insoluble in salt solution. 2 : 3'-Ethoxynaphthalenesulphonic acid is equally easily prepared; its sodium salt is sparingly soluble in water. Both compounds lose ethyl and become naphtholsulphonic acids when treated with anhydrosulphuric acid.
A. G. B.

Isomeric Nitrochloronaphthalenesulphonic acids. By P. T. CLEVE (*Chem. Centr.*, 1893, ii, 919—920; from *Öfvers K. Svenska Vet. Ak. Förh.*, 1893. 329).—As the result of his experiments on substituted naphthalenes, the author gives the following rules of substitution as trustworthy, except in such cases as clearly depend on a secondary rearrangement of the very mobile SO_3H group. (1) If the α - (or 1-) position is occupied by OH, NH, COMe, NH_2 , Cl, or Br, the new radicle will enter the position 2 or 4 (occasionally 4'). (2) If the α -position is occupied by CN, NO_2 , SO_3H , or COOH, the new radicle will enter the position 4' or 1' (occasionally 4). (3) If the β - (or 2-) position is occupied by OH, NH, or COMe, the new radicle will enter the position 1. (4) If the β -position is occupied by NH_2 , Cl, Br, I, or SO_3H , the new radicle will enter the position 4' or 1'. (5) The group SO_2Cl in the α - or β -position predisposes the entry of the NO_2 group into an α -position of the second ring.

The following table summarises the properties of the derivatives of the 14 nitrochloronaphthalenesulphonic acids which the author has obtained.

Constitution.	Chloride.	Amide.	Ethyl salt.	Constitution.	Chloride.	Amide.	Ethyl salt.
	m. p.	m. p.	m. p.		m. p.	m. p.	m. p.
1 : 2 : 4'	112°	214°	110°	1 : 4' : 1'	150°	233°	—
1 : 2 : 3'	161	203	139	1 : 1' : 4' } ?	134	—	—
1 : 2 : 2'	219	247	184	1 : 4 : 1' }	—	—	—
1 : 2 : 1'	190	226	181	1 : 1' : 2	129	245	124°
1 : 4 : 3'	116° (108°)	208	89	1 : 1' : 4'	127	181	—
1 : 4 : 2'	161°	188	123	2 : 1 : 4'	118	220	—
1 : 4' : 3'	151	220	116	2 : 1' : 2'	182	231	—
1 : 4' : 2'	130	188	—	—	—	—	—

Of the 33 possible trichloronaphthalenes, 16 have been obtained by the author and others, their melting points being as follows:—1 : 2 : 3 = 81°, 1 : 2 : 4 = 92°, 1 : 2 : 4' about 76°, 1 : 2 : 3' about 91°, 1 : 2 : 2' about 80°, 1 : 2 : 1' = 83°, 1 : 3 : 4' = 103°, 1 : 3 : 3' = 80°, 1 : 3 : 2' = 113°, 1 : 3 : 1' about 88°, 1 : 4 : 2' about 60°, 1 : 4 : 1' = 131°, 1 : 3' : 2' = 109.5°, 2 : 3' : 2' = 91°. Summaries of the properties and derivatives of the known dichloronaphthalenesulphonic acids, and of the mono- and di-chloronaphthalenes are also given.

L. T. T.

Orientation in the Terpene Series. By A. v. BAEYER (*Ber.*, 27, 436—454).—In the opening portion of this paper, the author deals with the nomenclature of the terpene series, which he models according to the rules agreed on at the Geneva Conference. The carbon

atoms in cymene are thus numbered.

$$\begin{array}{ccccccc}
 & 9 & & 5 & 6 & & \\
 & \text{C} & > & \text{C}-\text{C} & < & \text{C}-\text{C} & \\
 & 10 & & 8 & 4 & & 3 & 2 & & 1 & 7
 \end{array}$$

Wallach considers that dipentene is $\Delta 1 : 5$ -terpadiene (dihydro-cymene) on the ground of its optical activity, this being the only possible configuration containing an asymmetrical carbon atom; on

this assumption, however, he is compelled to admit that intramolecular change takes place when the hydrocarbon enters into combination with halogen hydrides. The author shows that when Wallach's terpineol dibromide (this vol., i, 44) is treated with a solution of hydrogen bromide in glacial acetic acid, 1 : 2 : 4-tribromoterpane (-hexahydrocymene) is produced, which, on bromination, is converted in dipentene tetrabromide (m. p. 124°). As the bromination is carried out in the cold, intramolecular change is inconceivable; it follows, therefore, that dipentene has not the constitution assigned to it by Wallach (see below).

When the tribromide (m. p. 110°) which Wallach obtained by brominating 1 : 4-dibromoterpane (-hexahydrocymene) is dissolved in glacial acetic acid, and treated at 0° with zinc dust, it yields a *terpenol* (terpineol) *acetate*, $C_{10}H_{17}OAc$, which forms a *dibromide* melting at 103°, and is converted, on hydrolysis with alcoholic potash, into a crystalline *terpenol* (terpineol) melting at 69—70°; the latter forms a *dibromide* melting at 114—115°. Both the terpenol and its acetate, if treated with a solution of hydrogen bromide in glacial acetic acid, yield *trans*-1 : 4-*dibromoterpene* (*dipentenedihydrobromide*), melting at 64°. If the dibromide of the terpenol, or of its acetate, is treated with hydrogen bromide in glacial acetic acid solution, Wallach's 1 : 4 : 8-tribromoterpane (m. p. 110°) is obtained. The terpenol acetate, like tetramethylethylene, forms a blue crystalline *nitroschloride* (compare Thiele, this vol., i, 217), melting at 80°. These facts indicate that the new terpenol has the constitution, $OH \cdot CMe < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} > C : CMe$. When the terpenol acetate is boiled with quinoline, terpinolene is obtained; terpinolene is, therefore, $\Delta^{1,4(9)}$ -terpadiene, $CMe \cdot C < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} > C : CMe$.

Dipentene is formed by the dehydration of solid terpenol (terpineol; this vol., i, 45), and the author finally concludes that it is $\Delta^{1,2}$ -terpadiene (dihydrocymene). Dipentene is, however, a racemic compound of two enantiomorphous substances, and is the first instance brought to light of such a compound not containing an asymmetrical carbon atom. The author also adduces evidence that the high-boiling terpinene is $\Delta^{1,5}$ -terpadiene, and the low-boiling terpinene, $\Delta^{3,5}$ -terpadiene. A. R. L.

Rose Oil. By J. BEETRAM and E. GILDEMEISTER (*J. pr. Chem.*, [2], 49, 185—196).—Monnet and Barbier (this vol., i, 141) state that they obtained rhodinol from geranium oil. The authors cannot isolate any rhodinol from the various commercial geranium oils. A reinvestigation of genuine rose oil shows that the geraniol from this source is identical with that from all other known sources. The variations in the sp. gr. of samples of geraniol are attributable to the ease with which the oil oxidises. A comparison of the properties and behaviour of the so-called rhodinol leads to the conclusion that this substance is a mixture consisting, for the most part, of geraniol, just as Barbier's licarhodol (*Abstr.*, 1893, i, 545) is an impure geraniol. What the impurity in geraniol which lends it the odour of roses may be

has yet to be settled. In spite of the statements of Markovnikoff and Reformatzky, stearoptene must still be regarded as a mixture of hydrocarbons. A. G. B.

Essential Oil of Lemon. By R. S. LADELL (*Chem. News*, 69, 20—21).—By fractional distillation of terpeneless oil of lemon, which is a mixture of several oxygenated compounds, the author has isolated a liquid having a constant composition approximating empirically to $C_{10}H_{18}O$, with a sp. gr. 0.962, and a specific rotatory power $[\alpha]_D = +6.42^\circ$; it boils at 206° . D. A. L.

Campholene. By GUERBET (*Compt. rend.*, 118, 286—288).—De-lalande's process of obtaining campholene by the action of phosphoric anhydride on campholic acid does not give a good yield. The best method is to distil campholic chloride in presence of a small quantity of phosphoric anhydride, when about 73 per cent. of the calculated quantity is obtained, and a single fractionation yields a pure product.

Campholene is a colourless liquid with a burning taste, and an odour similar to that of terebenthene; it boils at 134° under a pressure of 758 mm.; sp. gr. at $0^\circ = 0.8115$; vap. density, 4.26 (calc. 4.28). It is optically inactive, and when exposed to air slowly absorbs oxygen. Bromine attacks campholene violently at 0° with evolution of hydrogen bromide, but if the two substances are previously dissolved in 10 times their weight of chloroform, the bromine is absorbed quietly, and the absorption ceases when the two substances have been mixed in molecular proportion. There is practically no evolution of hydrogen bromide, but the product is very unstable, and gives off hydrogen bromide when the chloroform is evaporated. When treated with gaseous hydrogen iodide at 0° , campholene yields a crystalline compound, $C_9H_{16}HI$, which is very unstable.

When heated in sealed tubes at 280° with twice its volume of hydriodic acid saturated at 0° , campholene yields a hydrocarbon, C_9H_{16} , which boils at 132 — 134° ; sp. gr. at $0^\circ = 0.783$; vap. density 4.35. It does not combine with bromine, and is not attacked in the cold by fuming sulphuric acid or fuming nitric acid, but when heated for 10 days at 60 — 70° with a mixture of 2 vols. of fuming sulphuric acid and 1 vol. of fuming nitric acid, it yields a small quantity of a crystalline nitro-derivative with the same melting point as trinitropseudocumene. When treated with bromine in presence of aluminium bromide, it yields tribromopseudocumene.

It follows that the hydrocarbon, C_9H_{16} , is identical with the hexahydropseudocumene found in Baku petroleum, and, therefore, the campholene from which it is obtained must be regarded as tetrahydropseudocumene.

When sulphuric acid is agitated with one-third its weight of campholene, it rapidly blackens, and gives off sulphurous anhydride with development of heat. The products are the hexahydropseudocumene described above, and *dicampholene*, $C_{18}H_{32}$, an oily liquid which boils at 165 — 168° under a pressure of 30 mm., or, with partial decomposi-

tion, at 266—270° under ordinary pressure. It has an odour similar to that of terebenthene, and when exposed to air, oxidises somewhat rapidly with formation of resinous products.

It would seem that the compound obtained by Étard by the action of zinc chloride on α -chlorocamphor (Abstr., 1893, i, 524) cannot be campholene.
C. H. B.

Synthetic Borneols. By G. BOUCHARDAT and J. LAFONT (*Compt. rend.*, 118, 248—250).—Borneols of camphene are readily prepared by acting on the camphene with an equal weight of glacial acetic acid, in which has been dissolved one-third of its weight of sulphuric acid. The reaction proceeds quietly, but is almost instantaneous, and the conversion into borneol acetates is practically complete. A small quantity of a new compound is also formed, and is under investigation.

Camphene borneols form smaller crystals, and are more soluble in light petroleum than natural borneols or the borneols of terebenthene. The crystals sublime in the same way as camphor, but the borneols of terebenthene do not. Moreover, camphene borneols decompose into camphene and water if heated at 250° for 24 hours, and the decomposition is well marked, even at 225°, whereas terebenthene and dryabalanops borneols do not change under these conditions. It follows that the camphene borneols are isomeric with natural borneols, with those obtained from terebenthene, and with those having an unstable reversible rotatory power obtained by Montgolfier. On the other hand, when oxidised, they yield camphors identical with those from the other borneols.

In view of the large number of isomerides of compounds yielding identical derivatives, the authors consider that it is better to distinguish the different borneols according to their origin; for instance, camphene borneol, terebenthene borneol, rather than by such prefixes as *iso*, *para*, &c.
C. H. B.

Constitution of Cotoïn. By G. CIAMICIAN and P. SILBER (*Ber.*, 27, 409—426; compare Abstr., 1893, i, 718; this vol., i, 40, 51, 94).—Cotoïn, one of the constituents of the true Coto bark, has the formula $C_{14}H_{12}O_4$, and not $C_{22}H_{18}O_6$, as given by Jobst and Hesse. The diacetate, similarly, has the formula $C_{18}H_{16}O_6$, and, like cotoïn itself, contains a methoxy-group. When cotoïn is warmed with strong sulphuric acid, decomposition occurs, and a small amount of phloroglucinol is formed. This fact, and the general resemblance of cotoïn to hydrocotoïn (Abstr., 1891, 578), renders it probable that cotoïn is the monomethyl ether of benzoylphloroglucinol, $OMe \cdot C_6H_4(OH)_2 \cdot COPh$.

Dibromocotoïn, $C_{14}H_{10}Br_2O_4$, was described by Jobst and Hesse as tribromocotoïn. It forms large, prismatic, colourless needles, and melts at 116°. **Cotoïnozime**, $C_{14}H_{12}NO_4$, is obtained by adding hydroxylamine hydrochloride to a solution of cotoïn in cold aqueous sodium carbonate. It crystallises in plates, with a faint blue surface lustre. It is soluble in alcohol, slightly in water, readily in caustic alkalis. When cotoïn is treated with methylic iodide, it yields a *dimethylcotoïn*, $OH \cdot C_6H_4HMe(OMe)_2 \cdot COPh$, isomeric with the trimethylbenzoylphloro-

glucinol (dibenzoylhydrocoton) obtained by treating hydrocotoïn in the same manner. It separates from alcohol in crystals, melting at 138° . It forms yellow solutions in aqueous alkalis, and its solution in dilute alcohol gives a yellowish-brown coloration with ferric chloride. It only contains two methoxy-groups, and has, therefore, the constitution given above. Its *acetate* crystallises in white needles melting at 150° . It is insoluble in alkalis, and gives no coloration with ferric chloride.

It still remains to determine the relative positions of the methoxy- and benzoyl-groups in cotoïn.

When cotoïn is treated with acetic anhydride, the diacetate is accompanied by another compound, which forms lustrous prisms, melting at 142° . This substance is *methoxyhydroxyphenylcoumarin*

acetate, $\text{OMe}\cdot\text{C}_6\text{H}_4(\text{OAc}) < \begin{array}{c} \text{O}-\text{CO} \\ \text{CPh}\cdot\text{CH} \end{array}$; it is soluble in alcohol, but insoluble in alkalis, and, when hydrolysed, yields *methoxyhydroxyphenylcoumarin*, $\text{OMe}\cdot\text{C}_6\text{H}_4(\text{OH}) < \begin{array}{c} \text{O}-\text{CO} \\ \text{CPh}\cdot\text{CH} \end{array}$. The latter melts at

207° , and dissolves readily in alkalis. When this compound, or its acetate melting at 142° , is boiled with hydriodic acid, *metadihydroxyphenylcoumarin*, $\text{C}_6\text{H}_4(\text{OH})_2 < \begin{array}{c} \text{O}-\text{CO} \\ \text{CPh}\cdot\text{CH} \end{array}$, is obtained, melting at $233-234^{\circ}$, and being identical in every respect with the substance prepared synthetically by Kostanecki and Weber (this vol., i, 88). The *methoxyhydroxyphenylcoumarin* is not contained in the original cotoïn, but is formed from it by condensation with acetic acid.

The authors propose shortly to publish the results of their investigation of the so-called dicotoïn. A. H.

Constitution of Santonin. By S. CANNIZZARO (*Ber.*, 27, 530—536).—A polemical paper in answer to Klein.

Vitin and the Wax Compounds of American Grapes and their Hybrids. By W. SEIFERT (*Monatsh.*, 14, 719—738).—The grape berries, separated from the stalks, are treated with chloroform at the ordinary temperature for 2 to 8 days, and the chloroform extract is then separated from the juice and evaporated to dryness. The residue is extracted with water and then with absolute alcohol. It is thus separated into three substances: (1) soluble in cold alcohol; (2) soluble in hot alcohol but not in cold; (3) insoluble in alcohol.

Vitin crystallises from the cold alcoholic solution, when it is allowed to remain for some time. It is a white substance, crystallises in slender needles, and has no characteristic taste or odour. It is soluble in most organic solvents, dissolves in alkalis and sodium carbonate, and is reprecipitated by acids. It sinters, darkens, and then melts at $250-255^{\circ}$. The specific rotation $[\alpha]_D = +59.87$. The alcoholic solution has an acid reaction. Dilute acids have no action on the compound. It is partially dissolved by concentrated sulphuric acid, with an orange-red coloration, and is precipitated unchanged on

dilution. Concentrated nitric acid converts it into a resinous mass, which gives a deep red-brown solution with potassium carbonate, and has an intensely bitter taste. When heated with a small quantity of acetic anhydride, and then treated with concentrated sulphuric acid, a purple-red solution is obtained; the absorption spectrum of this solution shows a strong extinction between E and b, whilst the orange-red solution in sulphuric acid alone shows a dark band in the green between D and E and a continuous extinction from F into the blue and violet. If only a few drops of sulphuric acid are added to vitin which has been treated with acetic anhydride, a deep bluish-violet solution is obtained, which shows a faint extinction between C and D and a broad band at E. The author gives a table, showing the absorption spectra of vitin, abietic acid, and urson. The analysis and molecular weight determinations agree with the formula $C_{20}H_{31}O \cdot OH$. The *acetyl compound*, $C_{20}H_{31}O_2Ac$, crystallises in long needles, and sinters, darkens, and then melts at 239° . The *ammonium salt*, $C_{20}H_{31}O_2 \cdot NH_4$, $C_{20}H_{33}O_2$, crystallises in long needles. The *calcium salt* crystallises in long, slender needles, the *copper salt* is a bright blue powder consisting of microscopic needles. The *silver salt* is soluble in ether. Vitin does not reduce alkaline silver solution, and gives a negative result when tested for methoxyl by Zeisel's method. Therefore it contains neither an aldehyde- nor a methoxy-group.

An examination of those products obtained from the chloroform extract, which are insoluble in cold alcohol, showed that they contained wax-like compounds. The product, soluble in hot alcohol, melted at $69-70^\circ$, and contained myricyl alcohol and a fatty acid, melting at $75-80^\circ$, which, on analysis, gave numbers agreeing with the formula for cerotic or melissic acid. The product, insoluble in hot alcohol, melted at 72° , and contained an alcohol melting at 79° , and a fatty acid melting at $60-79^\circ$.

E. C. R.

Brazilin. By C. SCHALL (*Ber.*, 27, 524-530).—The author has already shown that brazilin contains four hydroxyl groups. He has obtained the tetramethoxy-compound, and finds it has the same melting point as the trimethoxy-compound.

Tetramethylbrazilin, $C_{18}H_{10}O(OMe)_4$, is obtained by heating the trimethoxy-compound with sodium and benzene at 120° , and then, after separating the excess of sodium, heating the product with methylic iodide at 120° . It may also be obtained by heating the trimethoxy-compound with methylic iodide and potassium hydroxide. It crystallises in white leaflets, does not decompose at $110-120^\circ$, and, when melted and suddenly cooled, is converted into an amorphous modification, which melts at $66-69^\circ$. It scarcely reddens when warmed with dilute nitric acid, and dissolves in concentrated sulphuric acid, from which solution it is not precipitated by the addition of water.

When the trimethylbrazilin is treated with ethylic iodide, it yields *methyltriethylbrazilin*, $OMe \cdot C_{18}H_{10}O(OEt)_3$, which crystallises in white needles, and melts at 149° .

Trimethylbrazilin, $C_{18}H_{11}O_3Me_3$, obtained as already described by the author, is very similar to the tetramethyl compound. The *acetyl*

derivative, $C_{18}H_{10}O(OMe)_2 \cdot OAc$, melts at $172-173^\circ$, and is easily hydrolysed by alcoholic potash.

Dimethylbrazilin, $C_{18}H_{12}O_2Me_2$, sinters at $75-80^\circ$, melts at $90-91^\circ$, and, when heated with methylic iodide and sodium ethoxide, is converted into trimethylbrazilin. When treated with acetic anhydride and sodium acetate, it yields a diacetyl derivative.

Methylbrazilin, $C_{18}H_{12}O_2Me$, is obtained by reducing the corresponding brazilein derivative with zinc-dust (*Ber.*, 22, 1560). It is a yellowish mass, which melts at 120° .

Tribromobrazilin yields a trimethyl compound, $C_{18}H_8Br_2O_2(OMe)_2$, which sinters at $100-105^\circ$, melts at $109-112^\circ$, and yields a monacetyl compound, melting at $179-180^\circ$.

Dibromobrazilin easily yields a monacetyl and a diacetyl derivative; the former melts at 170° and the latter at 245° .

When brazilin is heated with concentrated hydrochloric acid at 150° , it yields black compounds, soluble in alkalis; at 200° , it yields similar compounds, insoluble in alkalis. When heated with a large quantity of hydriodic acid and amorphous phosphorus at 200° , it yields an oil, which, on fractionation, furnishes hydrocarbons of the formulæ C_8H_{16} , b. p. $155-165^\circ$; $C_{10}H_{18}$, b. p. $170-175^\circ$; and $C_{11}H_{20}$, b. p. $180-185^\circ$. These hydrocarbons are colourless, or pale yellow, limpid liquids, and have a terpene-like odour.

E. C. R.

A Colouring Matter in Vine Leaves. By E. SCHUNCK, E. KNECHT, and L. MARCHLEWSKI (*Ber.*, 27, 487-488).—Brown vine leaves, gathered in the autumn, were found to contain, besides 2 per cent. of potassium hydrogen tartrate, a glucoside, which was obtained as a brownish-yellow substance, showing some semblance of crystalline structure. When boiled with dilute sulphuric acid, this glucoside yields sugar, and a colouring matter which was obtained as a reddish-brown powder, and dyes chrome- and tin-mordanted wool respectively brown and yellow.

C. F. B.

Glucose. By G. H. MORRIS (*Trans. Inst. Brew.*, 6, 132-142).—The author confirms Géduld's observation, that glucose which occurs in maize slowly hydrolyses dextrin, or perhaps, more correctly, the malto-dextrins to glucose. The author has examined the action of the cold water extracts of both germinated and ungerminated maize, barley, rye, oats, and wheat on maltose, but failed to detect the production of glucose, except in the case of maize. The reason that Lintner and Jalowetz were able to detect glucose in the product of the action on maltose of the cold-water extract of other cereals and of germinated grain, is that glucose pre-exists, ready formed in them. The author concludes that glucose is an enzyme peculiar to maize, or possibly common also to other unexamined cereals, but he does not believe that it is a normal constituent of barley or barley malt. It appears to him extremely doubtful whether it plays any part in the metabolism of the plant, or in the translocation of the carbohydrate material of this grain.

A. R. L.

Conversion of Pyrroline into Indole. By M. DENNSTEDT and F. VOIGTLÄNDER (*Ber.*, 27, 476—480).—Pyrroline is converted into tripyrroline by dissolving 25 c.c. in 100 c.c. of 20 per cent. hydrochloric acid, diluting with 500 c.c. of cold water, adding dilute ammonia, little by little, until no more precipitate forms, filtering, and shaking out the filtrate twice with ether. The ethereal extract, when evaporated, leaves a residue of tripyrroline, which at once crystallises. It is well to work as rapidly as possible. Tripyrroline, on keeping, is transformed into a higher polymeride, which is insoluble in ether, and melts at 121°. When tripyrroline is heated on the water bath, it loses 1 mol. of ammonia, and leaves a transparent brown residue, which, when heated to above 300°, breaks up into indole and pyrroline, the latter of which distils over first.

C. F. B.

Synthesis of Quinoline Derivatives. By S. NIEMENTOWSKI (*Chem. Centr.*, 1893, ii, 939; from *Anzeig. Akad. Wiss. Krakau*, 1893, 244). By the condensation of anthranilic acid with acetophenone, the author obtained phenylhydroxyquinoline [$\text{Ph} : \text{OH} = 2' : 4'$] (*Abstr.*, 1886, 812). By the condensation of metahomoanthranilic acid with acetophenone, α -phenyl- γ -hydroxymetatoluquinoline is formed. By the action of ethylic acetoacetate on anthranilic acid, γ -hydroxyquinaldine- β -carboxylic acid (Conrad and Limpach, *Abstr.*, 1888, 1110) is produced, together with a compound, $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_6$, which appears to be an anhydride of the former, and melts at 335°. From metahomoanthranilic acid and ethylic acetoacetate a compound, $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_6$, melting at 350°, is obtained. This, when treated with alkalis, takes up water, forming the substance $\text{C}_{12}\text{H}_{11}\text{NO}_3$, which melts at 248°, and is probably γ -hydroxy- α -methylmetatoluquinoline- β -carboxylic acid. Ethylic ethylacetoacetate yields, with anthranilic acid, a compound, $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_6$, melting at 286°, and with metahomoanthranilic acid, a compound, $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_6$, melting at 345°.

L. T. T.

Hydrogen Copper Quinolate. By I. BOESEKEN (*Rec. Trav. Chim.*, 12, 253—254).—When normal copper quinolate is boiled with nitric acid (sp. gr. 1.2), the salt, $\text{C}_{14}\text{H}_8\text{O}_4\text{Cu} + \text{H}_2\text{O}$, is obtained. It crystallises from nitric acid in bunches of blue needles, blackens at 258°, and cannot be dehydrated by heating without undergoing decomposition. One part of the salt dissolves in 4320 parts of water at 15°; the salt may perhaps serve for the detection of quinolinic acid.

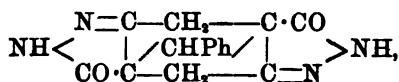
A. R. L.

1-Phenylpyrazolone. By F. STOLZ (*Ber.*, 27, 407—409).—Two distinct phenylpyrazolones are known, 1-phenyl-5-pyrazolone, melting at 118°, and 1-phenyl-3-pyrazolone, melting at 153°. Now, v. Rothenburg (*Ber.*, 26, 2974) describes a 1-phenyl-5-pyrazolone, melting at 154—155°. Some error must have been made here, since 1-phenyl-5-pyrazolone does not melt at 154—155°, but at 118°, and the reactions obtained by v. Rothenburg with his compound, melting at 154—155°, are not given by 1-phenyl-3-pyrazolone, which would appear from the melting point to have actually been the substance

obtained by him. It is not impossible that the confusion may have arisen from the formation of a mixture of the two pyrazolones.

A. H.

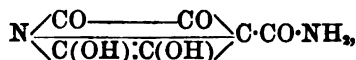
Ethyllic Succinosuccinate and Hydrazine. By R. v. ROTHENBURG (*Ber.*, 27, 471—473).—When ethyllic succinosuccinate (1 mol.) and hydrazine acetate or hydrate (2 mols.) are boiled together in alcoholic solution, they condense to *hexahydrobenzo-3:4-dipyrazolone*, $\text{NH} \begin{array}{c} \text{N}=\text{C}-\text{CH}_2-\text{CH}\cdot\text{CO} \\ \text{CO}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}=\text{N} \end{array} \text{NH}$, which crystallises in yellow prisms, and melts at 256—257°. When heated with benzaldehyde, it yields *hexahydrobenzo-4-benzal 3:4-dipyrazolone*,



a reddish-yellow powder, which is not melted at 280°. When heated with methylic iodide at 100°, it yields 1-*dimethylhexahydrobenzo-3:4-dipyrazolone*, $\text{NMe} \begin{array}{c} \text{N}=\text{C}-\text{CH}_2-\text{CH}\cdot\text{CO} \\ \text{CO}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}=\text{N} \end{array} \text{NMe}$, a yellowish powder melting above 250°; the corresponding ethyl derivative was also prepared, but was not obtained pure. When boiled with acetic anhydride, it yields 1-*diacetylhexahydrobenzo-3:4-dipyrazolone*, melting above 250°.

C. F. B.

Conversion of Citrazinamide into Phenylpyrazolonecarboxylic acid. By S. RUHEMANN and F. E. ALLHUSEN (*Ber.*, 27, 579—581).—The preparation of diketodihydroxyisonicotinamide,



has been previously described (*Abstr.*, 1888, 728). Attempts to obtain the corresponding acid were unsuccessful. On treatment with alkali, the compound is converted into ammonia, oxalic acid, and acetic acid. *Chlorocitrazinamide phenylhydrazone*,



is prepared by the action of phenylhydrazine on trichlorocitrazinamide, and crystallises in lustrous, yellowish-red plates. On heating with hydrochloric acid, it is hydrolysed with production of hydrogen chloride, oxalic acid, ammonia, and phenylpyrazolonecarboxylic acid,

$\text{NPh} \begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ | \\ \text{N}-\text{C}\cdot\text{COOH} \end{array}$ the formation of the latter being preceded by that of the intermediate compound,



This phenylpyrazolonecarboxylic acid is isomeric with the one previously described (*Trans.*, 1892, 799), and identical with the acid obtained by Wislicenus from ethylic oxalacetate and phenylhydrazine. The *silver salt* is gelatinous, and becomes granular on heating.

Chlorocitrazinamide phenylhydrazone dissolves in alkalis at ordinary temperatures with a dark red colour, and is precipitated unchanged on acidifying. By boiling with concentrated potash, ammonia is evolved, and *phenylhydrazonemethylhydroxyfumaric (maleic) acid*, $\text{COOH}\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{C}(\text{COOH})\cdot\text{C}(\text{OH})\cdot\text{COOH}$, is formed. The *dihydrogen potassium salt* is deposited in yellow crystals; it is unstable, and in aqueous solution readily decomposes into hydrogen potassium oxalate and 1-phenyl-5-pyrazolone-3-carboxylic acid. J. B. T.

Action of Aromatic Aldehydes on Parasubstituted Anilines. By O. KÜHLING (*Ber.*, 27, 567—572).—Paranitraniline condenses with benzaldehyde in alcoholic solution in the presence of hydrochloric acid, in the proportion of 2 mols. of the former to 3 of the latter, to form derivatives of dihydroimidazole. Parachloraniline and paramidophenol give similar products, but only in very small quantity, whilst substances such as paraphenylenediamine and its dimethyl derivative do not react, or are converted into resins.

Dinitropentaphenyldihydroimidazole, $\text{CHPh} < \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{CPh} \\ \text{N}(\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{CPh} \end{smallmatrix}$, is obtained from benzaldehyde and paranitraniline, and forms yellowish-white needles melting at 182—183°. It is insoluble in water, sparingly soluble in alcohol, and dissolves in hot hydrochloric acid, but separates on cooling, without change. It is not altered, even on boiling, by strong concentrated aqueous potash. When treated with tin and dilute hydrochloric acid, it is converted into the corresponding *amido-compound*, which forms long, yellowish needles, containing water of crystallisation. It is insoluble in water, readily soluble in alcohol, &c., and is not altered by alkalis. The anhydrous substance melts at 122—123°. The *hydrochloride* forms soft pointed needles.

Pentanitropentaphenyldihydroimidazole, $\text{C}_{33}\text{H}_{21}\text{N}_5\text{O}_{10}$, is prepared from paranitraniline and metanitrobenzaldehyde. It is insoluble in water, very sparingly soluble in alcohol, readily in benzene, and forms a white crystalline powder melting at 227—228°. It dissolves readily in concentrated hydrochloric acid, but is precipitated without change when the solution is diluted. An isomeric substance is obtained from paranitraniline and paranitrobenzaldehyde. It is scarcely soluble in benzene or concentrated hydrochloric acid, and is a yellowish-white, micro-crystalline powder, which does not melt below 290°.

A. H

Synthesis of α -Alkyl- β -naphthocinchonic acids: Specific Reaction for Aldehydes. By O. DOEBNER (*Her.*, 27, 352—354).—The formation of an α -alkyl- β -naphthocinchonic acid always takes place when an aldehyde (more than 1 mol.) and pyruvic acid (1 mol.) are dissolved in absolute alcohol, and β -naphthylamine (1 mol.), also dissolved in absolute alcohol, is added, the mixture being then heated for three hours on the water bath. The acid separates on cooling.

As pyruvic acid undergoes a partial decomposition into acetaldehyde and carbonic anhydride, a little of the α -methyl- β -naphthocinchonic acid (m. p. 310°) is formed, when no aldehyde is present in the substance to be tested.

The test does not apply to ketones, and is especially useful in determining the presence of the aldehyde group in ethereal oils. The sugars which are represented as aldehydes (glucose, galactose) do not give the test. J. W.

Rotatory Power of Coniine and its Salts. By F. ZECCHINI (*Gazzetta*, 23, ii, 601—607).—The author finds the specific rotation of coniine to be $[\alpha]_D = +13.51^\circ$ at 23° , a number agreeing closely with those given by former observers. In aqueous solution, its electrical conductivity is small, and of the same order as the conductivities of dimethylamine and diethylamine. Its molecular refraction at 23° was also determined for the rays D, H α , H β , and H γ .

$$M \frac{\mu_D - 1}{d} = 68.31. \quad M \frac{\mu_D^2 - 1}{d(\mu_D^2 + 2)} = 40.72.$$

Coniine has a much smaller rotatory power in benzene, alcoholic, or aqueous solutions than when undiluted. The acetate, hydrochloride, and hydrobromide, are optically active in alcoholic or benzene solutions, the two latter salts having the same rotatory power in alcohol; $[\alpha]_D = +4.42^\circ$. It is, however, very doubtful whether the salts are optically active in aqueous solutions, very small rotations being observed. W. J. P.

Strychnine Nitrate. By GUIGNES (*J. Pharm.*, [5], 29, 24—26).—The product obtained by dissolving strychnine in cold or warm dilute nitric acid, and evaporating the solution, is invariably coloured; if, however, the alkaloid is suspended in hot water, and dilute nitric acid (1 : 5) added drop by drop until the liquid is neutral and dissolution complete, a colourless product is obtained on evaporation. The crystals are anhydrous. Brucine nitrate remains in the mother liquor. JN. W.

Isomeride of Cinchonine. By E. JUNGLEISCH and E. LÉGER (*Compt. rend.*, 118, 29—32).—When the dihydrobromide of hydrobromocinchonine is treated with alcoholic potash, as in the process of Comstock and Koenigs, the products are cinchoniline, cinchonifine, apocinchonine, and a small quantity of a new isomeride which the authors call δ -cinchonine. With free hydrobromocinchonine, the products are the same, but the proportion of apocinchonine is somewhat higher. δ -Cinchonine is separated from cinchoniline by means of the lower relative solubility of its hydrochloride and the greater relative solubility of the compound of its hydrochloride with zinc chloride.

δ -Cinchonine separates from a slightly supersaturated ethereal solution in very long prisms, insoluble in water, but extremely soluble in alcohol, benzene, chloroform, and acetone, even at the ordinary temperature. Ether readily dissolves the base at the moment of its liberation from its salts, but gradually deposits it in long needles, which are only slightly soluble in the same solvent. δ -Cinchonine melts at 150° ; its specific rotatory power in alcoholic solution at 17° is $[\alpha]_D = +125.2^\circ$, in aqueous solution containing 2 mols. HCl, it is $[\alpha]_D = +176.9^\circ$, and with 4 mols. HCl, $+178.2^\circ$. Solutions of

the base and its salts become brown when exposed to air and light, yielding products much less alkaline than the base itself.

The salts of δ -cinchonine are, as a rule, very soluble, and crystallise badly, but the hydrochloride, hydrobromide, and basic oxalate are less soluble, and crystallise readily. The hydrochloride forms small, colourless, highly refractive prisms containing $1\frac{1}{2}\text{H}_2\text{O}$; the hydrobromide forms similar crystals containing $2\text{H}_2\text{O}$, and the basic oxalate forms slender, colourless needles containing $5\text{H}_2\text{O}$. C. H. B.

Aconitine. By M. FREUND and P. BECK (*Ber.*, 27, 433—436).—The authors state that they have made 14 carbon and hydrogen determinations of crystallised aconitine, the results of which, together with other considerations mentioned below, lead them to adopt the formula $\text{C}_{34}\text{H}_{47}\text{NO}_{11}$, instead of that ascribed to the alkaloid by Dunstan and his pupils, namely $\text{C}_{33}\text{H}_{46}\text{NO}_{11}$.

Ehrenberg and Pürfürst (*Abstr.*, 1892, 1254) regarded the substance obtained by boiling aconitine with water as a mixture of the benzoates of two bases; the authors have obtained a homogenous compound by repeatedly crystallising this product; it melts at $202\text{--}203^\circ$, and appears to have the formula $\text{C}_{36}\text{H}_{51}\text{NO}_{13}$, being the benzoate of a base $\text{C}_{33}\text{H}_{46}\text{NO}_{10}$, derived from aconitine thus:— $\text{C}_{34}\text{H}_{47}\text{NO}_{11} + \text{H}_2\text{O} = \text{CH}_3\cdot\text{COOH} + \text{C}_{33}\text{H}_{46}\text{NO}_{10}$. The authors have examined the salts of the last-named base, and come to the conclusion that it is identical with Dunstan's isaconitine; its properties also render it probable that it is identical with Wright's picraconitine, and they propose to retain Wright's name, picraconitine, for this base. Attempts to prepare aconitine by acetylating picraconitine have as yet yielded negative results.

It was stated above that when aconitine is boiled with water the benzoate of picraconitine is produced; another reaction proceeds concurrently, however, in which water is assimilated and benzoic and acetic acid formed together with a base $\text{C}_{25}\text{H}_{41}\text{NO}_9$. This base is also obtained by boiling picraconitine with alcoholic potash; it has all the properties of aconine. Since, therefore, aconitine appears to be acetylbenzoylaconine (compare Dunstan and Carr, *Trans.*, 1894, 290), Dunstan and Passmore's observation (*Trans.*, 1892, 401) that apo-aconine is formed by benzoylating aconine must be regarded as doubtful.

A. R. L.

[*Note.*—Dunstan (*Ber.*, 27, 664), in reply to Freund and Beck, points out that he and his collaborateurs have already shown (*Trans.*, 1894, 174, 290, &c.), that aconitine, on hydrolysis, yields acetic acid and "isaconitine," and that the latter is identical with Wright's "picraconitine." He has also proved that isaconitine is benzoylaconine, and therefore not isomeric with aconitine.—EDITORS.]

Action of Halogen acids on Fibrin. By J. BROD (*Chem. Centr.*, 1893, ii, 1065; from *Centr. Physiol.*, 7, 410—411).—The swelling of fibrin produced by weak hydrochloric acid increases with its concentration up to 0.8—0.9 per cent. and then diminishes. Hydrobromic acid produces less effect, and hydriodic acid less still. The hydrochloric acid present is in three conditions: (1) in combination with the calcium of the fibrin; (2) adherent, or loosely combined

with the fibrin; and (3) free. The swelling of the fibrin is greatest when the acid is present in about equal proportion in each condition.

W. D. H.

Eserine. By A. PETIT and M. POLONOVSKY (*J. Pharm.*, [5], 29, 55—59).—Eserine or physostygmine, $C_{15}H_{21}N_3O_8$, the active principle of the Calabar bean, crystallises from benzene in large, well-defined, flat prisms, and melts at 105—106°, and not at 69° as commonly stated; the sp. rotatory power in chloroform solution is $[\alpha]_D = -82^\circ$, in 98 per cent. alcoholic solution, -89° , and in benzene or toluene solution, -120° . The *benzoate*, which is quite stable, crystallises in small, hard, white prisms, and melts at 115—116°; the sp. rotatory power in 98 per cent. alcoholic solution is $[\alpha]_D = 98.1^\circ$. The *parahydroxytoluate* is very hygroscopic. The *metahydroxytoluate* resembles the benzoate, and melts at 156—157°; the sp. rotatory power in 98 per cent. alcoholic solution is $[\alpha]_D = -79.6^\circ$. The *acid citrate* forms a very hygroscopic, crystalline, white powder; the sp. rotatory power in alcoholic solution is $[\alpha]_D = -74.5^\circ$. The *normal tartrate* forms very deliquescent, microscopic crystals of the cubic system. The *methiodide*, $C_{15}H_{21}N_3O_8 \cdot MeI$, crystallises in small, pale-yellow, very deliquescent prisms, and melts with decomposition at about 100°; the sp. rotatory power in 98 per cent. alcoholic solution is $[\alpha]_D = -110^\circ$.

JN. W.

Active Principle of *Dorstenia Contrayerva*. By U. MUSSI (*L'Orosi*, 16, 259—263).—The author has examined the roots of the *Dorstenia contrayerva*, a Brazilian plant which is used as an antidote to the poison of serpents and as an antiseptic; he has extracted from it two amorphous substances which he terms *cajapin* and *contrayervine*, the reactions of which are given. The latter substance yields a white, amorphous *tartrate*. No analyses are given.

W. J. P.

Ovomucoid. By C. T. MÖRNER (*Zeit. physiol. Chem.*, 18, 525—552).—This is the name given to a proteid-like substance which can be obtained from white of egg, after boiling, acidifying, and filtering to separate albumin and globulin. Neumeister called it pseudo-peptone. It contains only 12.65 per cent. of nitrogen, and yields a reducing substance on boiling with dilute hydrochloric acid; on concentrating its solutions slowly, they become gummy.

W. D. H.

Atmid-albumoses. By R. H. CHITTENDEN and F. S. MEARA (*J. Physiol.*, 15, 501—534; compare Neumeister, *Abstr.*, 1889, 910).—The experiments show that the action of superheated water on coagulated egg-albumin is essentially a hydration process, and is accompanied by cleavages of much the same order as those met with in ordinary proteolytic digestion, giving rise, on the one hand, to a resistant substance of the anti-group, only a part of which passes into albumoses by repeated cleavage of the molecule, and, on the other hand, to a more readily hydrated main-group which passes through primary and secondary albumoses into peptone, which, in turn, is broken down into leucine and tyrosine.

W. D. H.

Organic Chemistry.

Action of Nitric Acid on Saturated Hydrocarbons. By M. KONOVALOFF (*J. Russ. Chem. Soc.*, **25**, 472—500; compare this vol., i, 159).—Normal hexane was subjected to the action of nitric acid under the same conditions as were employed by the author in his previous research on the nitration of nononaphthene. Nitric acid of sp. gr. 1.155 nitrates hexane at 115—120°, but the yield of mononitrohexane is bad; acid of sp. gr. 1.075 gives a yield equal to 60 per cent. of the theoretical if the temperature is raised to 140°, the *nitrohexane* formed in this way being nearly pure. It is a colourless liquid, which boils at 176° (corr.), under a pressure of 758 mm., and has the sp. gr. 0.9509 at 0°/0°, or 0.9357 at 20°/0°. Its molecular refraction (Lorentz) is 35.26, and its odour resembles that of aniseed. When boiled with strong soda, it dissolves, and on reduction with zinc-dust and acetic acid, it gives methyl butyl ketone and normal β -hexylamine. Bromine attacks it with formation of *bromonitrohexane*, $C_6H_{13}BrNO_2$, which is a heavy, colourless liquid, volatile in a current of steam; the density is 1.3616 at 20°/0°, and the molecular refraction 42.84. From the behaviour indicated above, it would appear that the nitrohexane formed by the direct nitration of normal hexane is *methylbutylnitromethane*.

Similarly a secondary mononitro derivative, *methylamylnitromethane*, is obtained by nitrating normal heptane with nitric acid of sp. gr. 1.075 at 125—130°. It boils at 194—196°, and has the density 0.9306 at 20°/0°. The corresponding *amine* boils at 141.5° under a pressure of 761 mm., and its sp. gr. is 0.7655 at 20°/0°.

By treating normal octane with nitric acid of sp. gr. 1.075 at 130°, the author obtained a fair yield of *methylheptylnitromethane*, distilling at 210—212° under atmospheric pressure, and at 123—124° under 40 mm. pressure. The sp. gr. of this nitro product was found to be 0.9201 at 20°/0°, and its molecular refraction 44.56. The corresponding *amine* boils at 163—164° under 754 mm. pressure, and its sp. gr. = 0.7745 at 20°/0°. J. W.

Suberone. By V. MARKOVNIKOFF (*J. Russ. Chem. Soc.*, **25**, 547—564).—Suberylic iodide and dilute hydrochloric acid were poured on to zinc which had been previously treated with a solution of copper sulphate. From time to time, concentrated hydrochloric acid was added, until the reduction of the iodide was complete. To purify the hydrocarbon thus obtained, it was distilled in a current of steam, treated with bromine to remove unsaturated hydrocarbons, and again distilled in a current of steam until the residue was heavier than water. The purified *suberene* (or heptamethylene, "suberane") boils at 117—117.5° under 743 mm. pressure, and its sp. gr. = 0.8094 at 20°/20°.

When allowed to remain for several days in a sealed tube with bromine and aluminium bromide, suberene is first converted into the

isomeric heptanaphthene, and then into pentabromotoluene. Hydriodic acid, in quantity insufficient for reduction, also effects the isomeric transformation into heptanaphthene at 250°.

Suberylene, C_7H_{12} , is obtained when a mixture of equal volumes of suberylic iodide and alcohol is added to strong alcoholic potash. It boils at 114·5—115° (corr.), and its sp. gr. = 0·8245 at 20°/20°.

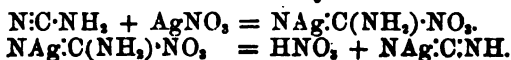
Suberone easily dissolves in nitric acid of sp. gr. 1·30, but there is no action until the solution is warmed. The only crystalline oxidation product obtained was normal pimelic acid. J. W.

Sulphur Compounds in Ohio Petroleum. By C. F. MABERY and A. W. SMITH (*Amer. Chem. J.*, 16, 83—89).—In this communication the authors defend the work described in their former paper (*Abstr.*, 1890, 350) against the criticism of Kast and Lagai (*Dingl. polyt. J.*, 284, 69), and express their belief that the petroleum examined by the latter were probably not Ohio oils. L. T. T.

Examination of Canadian Sulphur-petroleum. By C. F. MABERY (*Amer. Chem. J.*, 16, 89—93).—The crude petroleum examined had a sp. gr. of 0·86 at 20°, was rather thicker than Ohio crude petroleum, and had a slight odour of hydrogen sulphide. It contained 0·98 per cent. sulphur, and, when distilled under 250 mm. pressure, yielded 11 per cent. under 150°, containing 0·5 per cent. of sulphur; 24 per cent. between 150° and 300° (or burning oil), containing 0·64 per cent. of sulphur; and 65 per cent. of residue above 300° containing 0·98 per cent. of sulphur. Small quantities of hydrogen sulphide were evolved during the distillation.

A preliminary examination of the sulphur oils—obtained by decomposing some of the "sludge acid" obtained in refining the burning oil distillate—showed the presence of unsaturated hydrocarbons, more or less sulphuretted, the sulphur contained in the steam-distilled product, varying from 0·43 per cent. in the fraction 32—40° to 13·93 in the fraction 160—170°. The lower fractions (principally containing the unsaturated hydrocarbons) showed a great tendency to polymerise. The original sludge sulphur-oil had a sp. gr. of 0·86, and contained 9·94 per cent. of sulphur. The author is continuing his investigations on larger quantities of this oil. L. T. T.

Isomerism in the Cyanogen Series. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, 25, 456—466).—The author considers that most of the cyanogen compounds are of the type $X\cdot C\equiv N$, and that these enter more readily into actions involving direct addition than into double decompositions. The formation of compounds of the type $X\cdot N\equiv C$, he explains in accordance with this view by assuming that there is first direct addition between a molecule $X\cdot C\equiv N$, and a molecule of the reagent, after which there is a decomposition, with formation of a substance belonging to the type $X\cdot N\equiv C$ or $X\cdot N\equiv C\cdot X$. Thus he represents the action of silver nitrate or cyanamide as follows:



J. W.

Crystalline Form of Potassium Isocyanate. By R. OTTO (*Ber.*, 27, 837—838).—This salt crystallises in broad tablets, or small pyramidal crystals with a vitreous lustre. These are formed by the combination of a pyramid (111) with the plane (001), and the tablets are developed parallel to the last of these. The crystals belong to the quadratic system, and have the following constants. Axial ratio, $a : b : c = 1 : 1 : 0.5766$. Angles, (111) : ($\bar{1}11$), $78^{\circ} 22'$; (111) : ($\bar{1}\bar{1}1$), $53^{\circ} 8'$. The double refraction is very well marked and positive. No cleavage was observed.

From these measurements, it appears that the salt is isomorphous with thallium thiocyanate. A. H.

Derivatives of Acetonitrile. By W. ESCHWEILER (*Annalen*, 278, 229—239).—*Imidoacetonitrile*, $\text{NH}(\text{CH}_2\text{CN})_2$, is formed when an aqueous solution of hexamethylenamine is mixed with hydrogen cyanide (6 mols.), preferably in presence of 2 per cent. of hydrochloric or sulphuric acid; it crystallises from ether in colourless plates, melts at 75° , and decomposes above its melting point, giving rise to the odour of hydrogen cyanide and pyridine. If boiled with silver nitrate, silver cyanide is precipitated; Urech (*Ber.*, 6, 1116) has observed the same reaction with its homologue. The *hydrochloride* crystallises in delicate needles. When imidoacetonitrile is boiled with barium hydroxide solution, diglycollamidic acid is obtained; this melts with decomposition at 225° ; a small quantity of glycocine is also produced.

Nitriloacetonitrile, $\text{N}(\text{CH}_2\text{CN})_3$, is obtained when hexamethylenamine (100 grams) in water (500 c.c.) is mixed with 40 per cent. hydrogen cyanide (120 grams), and 35 per cent. hydrochloric acid (450 c.c.). It crystallises from water or alcohol in prisms or long needles respectively, melts at 126° , and yields triglycollamidic acid when boiled with barium hydroxide; if, however, it is heated in a sealed tube with hydrochloric acid at 150° , diglycollamidic acid is formed; in both cases a small amount of glycocine is produced.

Amidoacetonitrile is obtained, together with glycocine, by the action of ammonia on methylenecyanhydrin; when a large excess of ammonia is made use of, glycocine in almost theoretical yield is formed, whilst by the use of a very small quantity of ammonia, imidoacetonitrile and nitriloacetonitrile are the products. The last-named compound is readily prepared by adding rather more than 1 molecular proportion of fuming hydrochloric acid to a 35—40 per cent. solution of formaldehyde, and slowly dripping into the mixture a concentrated solution of potassium cyanide (1 mol.). Glycocine may be prepared by mixing equivalent quantities of potassium cyanide and ammonium sulphate, adding the calculated quantity of formaldehyde, and hydrolysing after some hours. The yield does not exceed 20 per cent. of the theoretical. A. R. L.

Amidophosphoric acid. By H. N. STOKES (*Amer. Chem. J.*, 16, 154—155).—When ethylic chlorophosphate was treated with dry ammonia at 0° until no further increase in weight occurred, the gain in weight was 17.2 per cent., and about 20 per cent. of monamido-

phosphoric acid was isolated from the product. The reaction $\text{POCl}(\text{OEt})_2 + 2\text{NH}_3 = \text{NH}_2\cdot\text{PO}(\text{OEt})_2 + \text{NH}_4\text{Cl}$, requires 19·8 per cent. increase, that of $2\text{POCl}(\text{OEt})_2 + 3\text{NH}_3 = \text{NH}[\text{PO}(\text{OEt})_2]_2 + 2\text{NH}_4\text{Cl}$ 14·8 per cent. The observed reaction therefore took place according to both equations. When the action was carried on at 100° , ethylic chloride was evolved in large quantities, a loss of 15·8 per cent. was observed and a solid residue dissolving slowly in water was left. The action is probably expressed by the equation, $\text{POCl}(\text{OEt})_2 + 2\text{NH}_3 = \text{NH}_2\cdot\text{PO}(\text{ONH}_2)\cdot\text{OEt} + \text{EtCl}$, requiring a loss of 17·7 per cent. L. T. T.

Multirotaion of Sugars. By P. T. MULLER (*Compt. rend.*, 118, 425—428).—The law that governs the well-known variation in the rotatory power of sugar solutions can be ascertained on the assumption that the solution contains only two modifications of the sugar, each with its own specific rotatory power. If x represents the mass and α_p the rotatory power of the unstable modification A, and y represents the mass and ρ the rotatory power of the stable modification B, p the number of grams of dissolved matter, V the volume in cubic centimetres, l the length of the column in decimetres, and α the angle of rotation at the end of the time θ , then

$$\alpha = [(a - 1)x + p] \frac{\rho l}{V},$$

and if the final angle α_n is introduced, it can be shown that

$$\alpha = \alpha_n \left[1 + \frac{(a - 1)x}{p} \right] \text{ or } \frac{(a - 1)x}{p} = \frac{\alpha}{\alpha_n} - 1,$$

which gives the quantity of the unstable modification x transformed in the time θ . Assuming that the quantity dx transformed in the time $d\theta$ is proportional to the mass of x present

$$dx = -C'x d\theta,$$

where C' is a constant positive factor, and by integration, x_0 being the quantity transformed in time θ_0 (corresponding with a rotation α_0) it follows that

$$C = \frac{1}{\theta - \theta_0} \log \frac{\alpha_0 - \alpha_n}{\alpha - \alpha_n}.$$

By means of the results of Parcus and Tollens, the author has calculated the values of C and $\frac{\alpha_0}{\alpha_n}$ for the following sugars:—

	C .	$\frac{\alpha_0}{\alpha_n}$.
Arabinose	0·0297	1·7585
Xylose	0·0201	4·77
Rhamnose	0·0393	—
Fucose	0·0202	1·742
Galactose	0·00950	1·531
Lactose	0·00409	1·608
Maltose	0·00553	0·362

In the case of glucose, the data are at present insufficient.

C. H. B.

Formation of Mannitol in Wines. By H. MALBOT and A. MALBOT (*Bull. Soc. Chim.*, [3], 11, 87—89).—An historical introduction. The paper is to be continued.

Action of Bases on Glucoses. By L. JESSEE (*Chem. Centr.*, 1894, i, 20—22; from *Österr-ung Zeit. Zucker-Ind. Landw.*, 22, 661—667; compare this vol., i, 4).—Baryta acts on invert sugar like calcium oxide; the acidity of the acids obtained from 2 mols. of the sugar is equivalent to $1\frac{1}{2}$ mol. of baryta, and they liberate carbonic anhydride from alkaline carbonates. The quantity of carbonic anhydride evolved on heating calcium hydroxide with levulose and invert sugar stands in molecular relationship to the amount of the levulose; practically none is evolved from the glucose (dextrose). The decomposition products of invert sugar, on titration in acid solution, exert no action on indicators, but on boiling with alkalis and acidifying, acids are liberated which affect phenolphthaleïn considerably, litmus less, and corralin scarcely at all. These acids are neutralised by boiling with acids, and in their general relationship they show a striking similarity to γ -lactones. J. B. T.

Action of Baryta on Glucose and Levulose. By M. H. COURTONNE (*Bied. Centr.*, 23, 210; from *Sucrerie indig. et colon.*, 41, 156).—A neutral, colourless solution of invert sugar (17 grams in 100 c.c.) when slowly heated with an equivalent amount of baryta or strontia to the boiling point, gives an abundant, slightly coloured precipitate at 70° which disappears in a few minutes, yielding a strongly coloured solution which is not precipitated by carbonic anhydride, or reduced by copper solution. When twice or three times the amount of the bases are employed, the precipitate becomes brown and is only partly dissolved. In both cases, the invert sugar is completely destroyed.

The different results obtained by Beaudet, who found that glucose and levulose are not precipitated either by hot or by cold baryta, and by Beaufret, who found that glucose is partly precipitated and partly destroyed, were probably due to the strength of the solutions not having been taken into account. N. H. M.

Compounds of Sugars with Mercaptans. By E. FISCHER (*Ber.*, 27, 673—679).—The author has obtained a number of compounds of certain sugars with various mercaptans, which are termed mercaptals, they differ from the alcohol glucosides recently described (this vol., i, 3) in containing two molecules of mercaptan to one of sugar. *Glucose-ethylmercaptal*, $C_6H_{12}O_6(SET)_2$, is prepared by the addition of ethyl mercaptan to glucose dissolved in well-cooled hydrochloric acid (sp. gr. 1.19). The compound crystallises from water or absolute alcohol in slender, colourless needles, or thin plates, melts at 127—128° (uncorr.), and the refractive power $[\alpha]_D = -29.8$ at 50°. It undergoes considerable decomposition on distillation, the product having the odour of roasted onions. The mercaptal has a bitter taste, it does not react with phenylhydrazine, or alkaline copper solution, and is hydrolysed by dilute mineral acids, mercuric chloride, or

silver nitrate; it dissolves in alkalis and is reprecipitated unchanged on acidifying, bromine or nitrous acid cause its decomposition; on oxidation with potassium permanganate, an acid derivative of glucose is formed which contains sulphur. With concentrated hydrochloric acid, the mercaptal becomes red and gradually changes to an oily liquid which contains sulphur, is readily soluble in water, and does not reduce alkaline copper solution. The mercaptal is without physiological action. Hydrobromic acid (sp. gr. 1.49), nitric acid (sp. gr. 1.16), sulphuric acid (50 per cent.), zinc chloride solution (50 per cent.), or even dilute hydrochloric acid may be employed to cause the condensation of the mercaptan and glucose. The *sodium salt*, $C_{10}H_{21}S_2O_5Na$, crystallises in slender needles. The *potassium salt* has also been obtained, but attempts to prepare a methyl derivative led to no definite results.

Galactose-ethylmercaptal, $C_6H_{13}O_5(SEt)_2$, is prepared in a similar manner to the preceding compound which it closely resembles; it crystallises in slender, colourless needles, melts at $140-142^\circ$ (uncorr.), has a bitter taste and is lævogyrate. The yield is practically quantitative.

Arabinose-ethylmercaptal crystallises in colourless needles, melts at $124-126^\circ$, and is sparingly soluble in water.

Mannose-ethylmercaptal forms slender needles which soften at about 128° , and melt at $132-134^\circ$.

Rhamnose-ethylmercaptal crystallises in slender, lustrous plates or needles melting at $135-137^\circ$.

α -Glucoheptose-ethylmercaptal melts at $152-154^\circ$.

Xylose, lactose, and maltose also combine with ethylmercaptan, but the products are oily. *Glucose-amymercaptal*, $C_6H_{13}O_5(SC_2H_5)_2$, is prepared from commercial amyl mercaptan in a manner similar to the ethyl derivative and probably consists of two isomerides, it is almost insoluble in cold water, crystallises from alcohol in slender needles, melts at $138-142^\circ$, and is hydrolysed by warming with dilute hydrochloric acid.

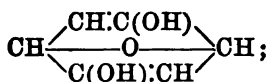
The following crystalline compounds have also been prepared:—*galactose-amymercaptal*, *arabinose-amymercaptal*, *glucose-benzylmercaptal*, $C_6H_{13}O_5(SCH_2Ph)_2$, and *galactose-benzylmercaptal*; *xylose-amymercaptal* is a viscid liquid. The author points out that these amymercaptals could be advantageously employed for the detection and isolation of various sugars, on account of the readiness with which they are formed and of their sparing solubility.

Corresponding derivatives of thiophenol and of hydrogen sulphide could not be obtained, neither does fructose or sorbose appear to form mercaptals.

J. B. T.

Maltol. By J. BRAND (*Ber.*, 27, 806—810).—Caramel colouring malt, which has recently been introduced into the brewing and malt industry, is prepared by roasting malt which contains a large proportion of water; it differs, therefore, from ordinary colouring malt in possessing a considerably higher percentage of sugar. Beer, prepared from caramel malt, gives a violet coloration with ferric chloride; this is not due to salicylic acid, but to the presence of a com-

pound termed *maltol*, which is distinguished from salicylic acid by giving no reaction with Millon's reagent. The temperature employed in the manufacture of malt coffee is higher than that used in the preparation of caramel malt, and in this case maltol is formed in larger quantity, and can be isolated from the volatile products in the manner described in the original paper. Maltol readily sublimes, and is deposited in colourless, odourless crystals melting at 159°. It has the characteristic properties of a phenol, does not form an oxime or a phenylhydrazone, reduces silver solutions at ordinary temperatures, and alkaline copper solution on heating. Maltol is probably a condensation product of grape sugar, and has the formula



this formula most readily accounts for its properties, and agrees with the analytical results and molecular weight determination.

J. B. T.

Action of Ethylenic, Propylenic, Isobutylenic, Pseudobutylenic, and Amylenic Bromides on Trimethylamine. By G. KLEINE (*Chem. Centr.*, 1894, i, 16—18; from *Zeit. Naturw.*, 66, 1—72).—It is known that only primary monobromo-substituted hydrocarbons form additive compounds with amines; secondary and tertiary derivatives yield unsaturated hydrocarbons and hydrogen bromide. The author finds that in the case of dibromo-hydrocarbon derivatives those alone form additive compounds with trimethylamine which contain the bromine linked to two primary carbon atoms.

The following compounds are formed by the action of isobutylenic bromide on trimethylamine: Trimethylamine hydrobromide, isocrotylic bromide, $\text{CHBr} \cdot \text{CMe}_2$ (b. p. 90—92°); and *isocrotyltrimethylammonium bromide*, $\text{CMe}_2\text{CH} \cdot \text{NMe}_3\text{Br}$; this compound is homologous with neurine, which, like valeryltrimethylammonium chloride, it closely resembles in physiological action. *Dibromisobutyltrimethylammonium bromide* and *dibromisobutyltrimethylammonium dibromide* have also been prepared.

Trimethylamine and pseudobutylenic bromide in molecular proportion yield trimethylamine hydrobromide, but with 2 mols. of the base, pseudocrotylic bromide, $\text{C}_4\text{H}_7\text{Br}$ (b. p. 90—91.8°), and hexamethylpseudobutylenediamine bromide, $\text{C}_6\text{H}_{12}\text{N}_2\text{Br}_2\text{Me}_6$, are also formed; the former in large, the latter in small quantity.

The following compounds are formed by the action of ethylenic bromide on trimethylamine in molecular proportion at 100° under pressure: *Tetramethylammonium bromide*, crystallising in colourless plates; trimethylamine-ethylenic bromide, $\text{C}_2\text{H}_4\text{Br} \cdot \text{NMe}_3\text{Br}$; trimethylamine hydrobromide in small quantity; a resinous aldehyde; hexamethylethylenediamine bromide, $\text{C}_2\text{H}_4\text{N}_2\text{Me}_6\text{Br}_2$; trimethylvinylammonium bromide (neurine bromide); dimethylamine bromide; aldehyde.

Propylenic bromide and trimethylamine at 100° yield: Trimethylamine hydrobromide; *β-propenyltrimethylammonium bromide*, $\text{C}_3\text{H}_5\text{NMe}_3\text{Br}$, a homologue of neurine; dimethylamine hydrobrom-

ide; and α -bromopropylene. Hydrogen bromide is eliminated by the action of trimethylamine (2 mols.) on propylene-bromide at the ordinary temperature.

Amylenic bromide (b. p. 74° under 15 mm. pressure) acts on trimethylamine at the ordinary temperature with formation of trimethylamine hydrobromide; at 100° , *valeryltrimethylammonium bromide*, $C_5H_9NMe_3Br$ (see above), is also produced, and combines directly with 10 atoms of bromine to form a perbromide.

J. B. T.

β -Ethylhydroxylamine. A correction. By J. W. BRÜHL (*Ber.*, 27, 805).—A reply to C. Kjellin (this vol., i, 223), whose claim to have independently isolated the β -alkylhydroxylamines is admitted.

J. B. T.

Action of Hydrazine Hydrate on Ethylic Cyanacetate and Malononitrile. By R. v. ROTHENBURG (*Ber.*, 27, 685—691).—Ethylic cyanacetoacetate readily combines with hydrazine hydrate to form *cyanacetylhydrazine*, $CN \cdot CH_2 \cdot CO \cdot NH \cdot NH_2$, which crystallises from alcohol in colourless prisms melting at 114.5 — 115° . It dissolves without decomposition in alkalis, alkali carbonates, and acids at ordinary temperatures; but, on heating, is hydrolysed into malonic acid, hydrazine, and ammonia. The yield of cyanacetylhydrazine is quantitative. Phenylhydrazine and hydrazine acetate do not act on ethylic cyanacetoacetate.

Cyanacetylbenzalhydrazine, $CN \cdot CH_2 \cdot CO \cdot NH \cdot N \cdot CHPh$, is obtained from the preceding compound by treatment with benzaldehyde, and crystallises from alcohol in colourless plates melting at 174.5° ; by acids or alkalis, it is resolved into its constituents.

Cyanacetylisopropylhydrazine, $CN \cdot CH_2 \cdot CO \cdot NH \cdot N \cdot CMe_3$, formed from cyanacetylhydrazine and acetone, resembles the benzal derivative; it crystallises in large, colourless, flat needles, and melts at 152° .

Cyanacetylorthohydroxybenzalhydrazine,



from cyanacetylhydrazine and salicylaldehyde, crystallises from alcohol in small, yellow needles, and melts at 169° .

Ethylic cyanacetylhydrazinepyruvate, $CN \cdot CH_2 \cdot CO \cdot NH \cdot N \cdot CMe \cdot COOEt$, is obtained by the action of ethylic pyruvate on the hydrazine; it is crystalline, and melts at 144° .

Ethylic cyanacetylhydrazineacetoacetate,



is prepared in a manner similar to the preceding compound, and crystallises in needles melting at 98° .

Cyanacetylacetylhydrazine, $CN \cdot CH_2 \cdot CO \cdot NH \cdot NHAc$, formed from acetic anhydride and the hydrazine, crystallises from alcohol, and melts at 172° .

Cyanacetylbenzenesulphonylhydrazine, $CN \cdot CH_2 \cdot CO \cdot NH \cdot NH \cdot SO_2Ph$, is formed by the action of benzenesulphonic chloride and soda on the hydrazine; it is crystalline, and melts at 176° .

Attempts to convert cyanacetylhydrazine or its compounds into pyrazolidone- or pyrazolone-derivatives were unsuccessful.

Symmetrical dicyanacetylhydrazine, $N_2H_2(CO \cdot CH_2 \cdot CN)_2$, is prepared by the action of iodine on cyanacetylhydrazine, or by heating the ethylic acetoacetate-derivative at 100° ; it forms granular crystals, and melts at 162° . A red, crystalline compound, which melts at 156° , and is probably *formazylie cyanide*, $CN \cdot C(N \cdot NHPh) \cdot N \cdot NPh$, is obtained by the action of diazobenzene chloride on ethylic cyanacetate in alkaline solution.

3:5-Diamidopyrazole, $NH < \begin{smallmatrix} N : C(NH_2) \\ C(NH_2) : CH \end{smallmatrix} >$, is formed by the interaction of hydrazine hydrate or acetate, and malononitrile at ordinary temperatures; it is a dark brown, oily liquid, and has not yet been purified; with ferric chloride, a violet dye is produced, which is sparingly soluble. The *picrate* crystallises in reddish plates, darkens at $230-240^\circ$, and decomposes at 250° .

3:5-Dibenzaldiamidopyrazole, $NH < \begin{smallmatrix} N : C(N \cdot CHPh) \\ C(N \cdot CHPh) : CH \end{smallmatrix} >$, is prepared by the action of benzaldehyde on the pyrazole; it crystallises with difficulty, and melts at about 170° .

Hydrazine picrate, $N_2H_4 \cdot C_6H_3N_3O_7$, is an extremely characteristic derivative of hydrazine; it crystallises from alcohol in pale yellow needles, melts at 184° , does not explode when heated on platinum foil, and is more sparingly soluble than phenylhydrazine picrate.

J. B. T.

The "Dinitroalkylic acids." By A. P. N. FRANCHIMONT and H. VAN ERP (*Rec. Trav. Chim.*, 12, 330-333).—Dilute sulphuric acid seems to have no action on the zinc or copper derivative of methyl-nitramine, other than liberating the amine. On treating Frankland's zinc or copper "dinitromethylate" in a similar manner, gas is evolved in small quantities, and a substance of higher melting point than methyl-nitramine is obtained. The authors are investigating these compounds.

W. J. P.

Complex Metallic Bases. By N. KURNAKOFF (*J. Russ. Chem. Soc.*, 25, 565-618).—When an aqueous solution of potassium chloroplatinite is added in excess to a solution of thiocarbamide at the ordinary temperature, the compounds $PtCl_2 \cdot 2CS(NH_2)_2$ and $PtCl_2 \cdot CS(NH_2)_2$ are precipitated, and on warming these with excess of thiocarbamide they are transformed into the soluble compound $PtCl_2 \cdot 4CS(NH_2)_2$, which is of the character of Reiset's first base. When a warm, concentrated solution of potassium chloroplatinite is poured into a warm, saturated solution of thiocarbamide, there is considerable development of heat, and the liquid, on cooling, deposits fine needles of the salt $PtCl_2 \cdot 4CS(NH_2)_2$. Hydrogen sulphide does not precipitate a solution of this salt, but the alkalis give amorphous orange precipitates. The compound is easily oxidized, the sulphur being converted into sulphuric acid. The corresponding bromide, sulphate, nitrate, chloroplatinate, and chloroplatinite were prepared from it.

The salt, $PtCl_2 \cdot 2CS(NH_2)_2$, unites with pyridine, forming the compound $PtCl_2 \cdot 2CS(NH_2)_2 \cdot 2C_5H_5N$.

The palladium compound, $PdCl_2 \cdot 4CS(NH_2)_2$, was obtained in an analogous manner to the corresponding platinum compound.

Substituted thiocarbamides give similar salts with 2 and 4 mols. of base to 1 mol. of platinous chloride. Mixed salts containing thiocarbamides and pyridine or ammonia can easily be prepared, various isomerides existing.

Thioacetamide forms analogous platinum bases, which are, however, less stable than the thiocarbamide bases, especially in presence of water. Xanthogenamide bases were also prepared.

The author discusses at considerable length the constitution of the compounds obtained by him. J. W.

Aliphatic Acids of Lanolin. By J. DE SANCTIS (*Gazzetta*, 24, i, 14—28).—Lanolin was treated with hot sodium ethoxide solution, and the sodium salts deposited were then extracted with ether to remove basic compounds. The acids not volatile in a current of steam were found to be cerotic, palmitic, normal caproic, and oleic acids. Those volatile in a current of steam were stearic, isovaleric, and normal butyric acids. The acids were separated by means of their lead salts, and analysed quantitatively. W. J. P.

Constitution of Ethylic Acetoacetate. By H. v. PECHMANN (*Annalen*, 278, 223—228).—One of the most weighty arguments advanced by Nef (*Abstr.*, 1893, i, 629) in support of the hydroxyl formula for ethylic acetoacetate is the formation by direct acetylation of the so-called ethylic β -acetisocrotonate. The author's experiments show that only traces of the acetoxy-compound are formed by protracted boiling of ethylic acetoacetate with a large excess of acetic anhydride (compare also Claisen, this vol., i, 31). Nef (*loc. cit.*) distils off most of the acetic anhydride from the product of the action, and shakes the residual oil with soda, the undissolved portion being ethylic β -acetisocrotonate. The author contends, therefore, that proof is wanting that this acetoxy-compound is produced by direct acetylation, for he has previously shown (*Ber.*, 25, 1046) that the same acetoxy-compound (ethylic triacetoacetate) is produced together with ethylic diacetoacetate, when ethylic acetoacetate is shaken with acetic anhydride and soda. A. R. L.

Pyruvic acid. By R. OTTO (*Ber.*, 27, 838).—The author has noticed the occurrence of pyruvic acid in a solution of tartaric acid which had been kept for some years exposed to light. The solution was dark yellow, and smelled of caramel. A. H.

Formation of Hydroxamic acids from Ethereal Salts. By A. HANTZSCH (*Ber.*, 27, 799—804).—The action of hydroxylamine on ethylic oxalacetate was investigated by the author some years ago, when a crystalline acid was obtained, from which a number of derivatives were prepared and analysed; on recently repeating the work, it was found that some unknown substance had been supplied instead of ethylic oxalacetate, and attempts to determine the nature of this substance led to the preparation of the compounds described below. Dihydroxamic acids are most conveniently obtained by dissolving the ethereal dicarboxylate in concentrated aqueous hydroxylamine solu-

tion, and adding concentrated alkali, or saturating the liquid with ammonia, the sparingly soluble ammonium or alkali salt is then decomposed by acids. Oxaldihydroxamic acid, $\text{NOH}\cdot\text{C}\cdot\text{C}\cdot\text{NOH}$, melts at 165° , instead of 105° , as stated by Lossen; the yield is quantitative. *Malonodihydroxamic acid*, $\text{CH}_2[\text{C}(\text{OH})\cdot\text{NOH}]_2$, crystallises from water in large, lustrous, prisms, melting at $154\text{--}155^\circ$ with violent decomposition; it is insoluble in ether, and has only a feebly acid action. The *ammonium salt*, $\text{C}_2\text{H}_5\text{N}_3\text{O}_4$, readily evolves ammonia, and melts at 141° with decomposition. The *copper salt* dissolves in excess of cupric acetate solution, but is insoluble in presence of sodium chloride, or ammonium chloride. *Ammonium malonhydroxamate*, $\text{NOH}\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{COONH}_4$, is prepared by prolonged boiling of the preceding ammonium salt in aqueous solution, and melts at 181° . The action of hydroxylamine on ethylic succinate and ethylic acetate is similar to its action on ethylic malonate, and will be described later.

J. B. T.

Constitution of Platoso-oxalyl Compounds. By H. G. SÖDERBAUM (*Zeit. Anorg. Chem.*, 6, 45—48).—Werner (*ibid.*, 3, 317) seeks to account, on stereochemical grounds, for the isomerism of the platoso-oxalyl compounds, originally prepared by the author. The validity of this explanation rests on the hypothesis that these compounds contain 2 mols. of water, which cannot be eliminated without decomposing the compounds. Whilst this is true of the ammonium derivatives, it is not true of the potassium derivatives, which lose their water without decomposition and show the same isomerism when anhydrous. Some light may be thrown on the isomerism by the fact that the dark potassium platoso-oxalyl compound gives an acid derivative, $\text{HK}_2\text{Pt}_2(\text{C}_2\text{O}_4)_2 + 6\text{H}_2\text{O}$, whilst the yellow variety gives no such derivative.

A. G. B.

Solubility of Metallic Oxides in Normal Potassium Salts of Tartaric and other Organic acids. By L. KAHLENBERG and H. W. HILLYER (*Amer. Chem. J.*, 16, 94—108).—Observing that when lead oxide is added to a boiling solution of normal potassium tartrate it is freely dissolved and the solution becomes alkaline owing to liberation of potassium hydroxide, the authors have investigated the action. Lead oxide is freely dissolved until the solution contains lead oxide and potassium tartrate in molecular proportion; beyond this point, solution takes place with difficulty only, but by long-continued boiling with pretty strong solutions of the tartrate, the authors succeeded in dissolving about 1.24 mol. proportions of lead oxide in 1 mol. proportion of potassium tartrate. Where the ratio of oxide to tartrate is one or more, only half the potassium in the tartrate is liberated as hydroxide. From a strong boiling solution containing excess of lead, a precipitate is formed, on cooling, which is a basic lead tartrate of the formula $(\text{PbO})_2\text{C}_4\text{H}_2\text{O}_6\text{Pb}$. From weaker solutions, alcohol causes a precipitate of the approximate composition Pb 56.5 per cent., K 10.6, C 9.2, H 0.9, which is probably a mixture of a tartrate of the proportion $\text{Pb}:\text{K} = 1:1$ with a more basic lead tartrate. When precipitated lead tartrate is treated with 2 mol. proportions of potash in

aqueous solution, the same potassium lead tartrate seems to be formed, as the lead tartrate is dissolved, and only half the potash remains in the free state. The normal tartrates of sodium, lithium, rubidium, and ammonium act like potassium tartrate, but thallium tartrate and potassium antimonyl tartrate do not act on lead oxide. When potassium ethylic tartrate is treated with lead oxide, it is saponified, but the resulting white lead salt goes into solution only on adding an alkali hydroxide. Hydrogen potassium tartrate acts on lead oxide like ethylic potassium tartrate, only much more slowly; the action is much accelerated by the addition of a little potassium hydroxide. The following oxides, As_2O_3 , Sb_2O_3 , SnO_2 , Bi_2O_3 , HgO , Ag_2O , Pb_3O_4 , CuO , Fe_2O_3 , Al_2O_3 , Cr_2O_3 , MnO_2 , ZnO , MgO , BeO , Er_2O_3 , Ce_2O_3 , Di_2O_3 , and UO_3 , were found to have no action on normal potassium tartrate.

Potassium malate, citrate, lactate, and glycerate take up but insignificant quantities of lead oxide, whilst potassium succinate, malonate, acetate, and propionate do not act on it. Potassium mucate and potassium saccharate act on lead oxide in a similar way to the tartrate, forming known basic salts of the probable formulæ $\text{C}_6\text{H}_4\text{O}_6\text{Pb}_2$. The reactions take place between 2 mols. of lead oxide and 1 of mucate or saccharate. From their results, the authors consider the following conclusions as probable:—1. In order that its normal potassium salt may react readily with lead oxide, the organic acid must be bibasic, and must contain two, or a multiple of two, alcoholic hydroxyl groups. 2. The number of molecules of the oxide with which 1 mol. of salt readily reacts is equal to one-half the number of alcoholic hydroxyl groups contained in the acid. L. T. T.

Preparation of Lead Triethide. By A. GHIRA (*Gazzetta*, 24, i, 42—45).—Löwig and Klippel (*Gmelin's Handbook*) gave a method for preparing lead triethide by the action of ethylic iodide on an amalgam of lead and sodium. Numerous attempts to prepare the substance have, however, failed, lead tetrethide being obtained instead; the author suggests that the difficulties met with in analysing the product are probably the cause of the error into which Löwig and Klippel fell. W. J. P.

Sulphonation of Thiophen and its Oxidation by Sulphuric acid to a new Dithienyl. By A. TÖHL (*Ber.*, 27, 665—667).—When thiophen (5 grams) is added to faintly fuming sulphuric acid (50 grams), well cooled with ice-cold water, and then subjected to steam distillation, a fairly good yield of a dithienyl isomeric with the compound obtained by Nahnsen, is obtained, and the remainder of the thiophen may be recovered from the acid solution as the barium or lead sulphonate.

The *dithienyl*, $\text{C}_8\text{H}_6\text{S}_2$, crystallises in large, colourless leaflets, melts at 33° , boils at 260° (uncorr.) under the ordinary pressure, without decomposition, and, with sulphuric acid, gives a yellow solution having a green fluorescence. When the solution in sulphuric acid is warmed with isatin, a beautiful bluish-violet coloration is produced.

Perbromodithienyl, $\text{C}_8\text{Br}_4\text{S}_2$, is obtained by warming dithienyl dis-

solved in acetic acid with excess of bromine. It crystallises in needles and melts at 257° (uncorr.).

Bromothiophen is also partially converted into bromodithienyl by the action of concentrated sulphuric acid, but other reactions also take place. Dibromothiophen yields a brominated dithienyl, dibromothiophensulphonic acid, sulphonic acids containing less bromine and tribromothiophen.

E. C. R.

Action of Nitric Acid on Aromatic Hydrocarbons. By M. KONOVALOFF (*J. Russ. Chem. Soc.*, 25, 509—546).—Benzene is scarcely attacked by nitric acid of sp. gr. 1.075 at $125\text{--}130^{\circ}$. Toluene, under the same conditions, gives benzoic acid, but, if heated with the acid for a long time at 105° , it gives small quantities of a nitro-compound boiling at 115° . Ethylbenzene, when heated with the acid at $105\text{--}110^{\circ}$, gives a yield of about 63 per cent. of an oil which decomposes when distilled even under reduced pressure.

The crystalline potassium salt obtained from the crude product may be purified by recrystallisation from alcohol. When carbonic anhydride is passed into its alcoholic solution, or when the salt is treated with dilute nitric, acetic, or sulphuric acid, a mixture of acetophenone and phenylnitroethane is formed. An aqueous solution of the potassium salt, however, when decomposed by a current of hydrogen sulphide yields pure *phenylnitroethane*, $\text{CHMePh}\cdot\text{NO}_2$. This is volatile in a current of steam, and under a pressure of 25 mm. distils at 135° without undergoing any appreciable decomposition. At the atmospheric pressure, it boils at $230\text{--}236^{\circ}$, but there is considerable decomposition. It is a colourless liquid, which does not crystallise at -15° ; its sp. gr. = 1.1202 at $20^{\circ}/0^{\circ}$, and its molecular refractive power is 41.379. In alkalis, it dissolves readily with formation of alkali salts which may be easily obtained in the crystalline form. Salts of the heavy metals give coloured precipitates with solutions of the sodium salt. Phenylnitroethane behaves as a secondary nitro-compound with nitrous acid. It is not attacked by bromine, but its potassium salt yields a *monobromide*, $\text{C}_6\text{H}_5\text{BrNO}_2$, which is a yellow oil having a sp. gr. of 1.5182 at $20^{\circ}/0^{\circ}$.

On reduction with zinc dust in alkaline solution, phenylnitroethane yields *α -phenylethylamine*, $\text{CHMePh}\cdot\text{NH}_2$, which boils at $186\text{--}189^{\circ}$. Its hydrochloride crystallises in long, flat needles, and melts at 155° .

Propylbenzene is attacked by nitric acid of sp. gr. 1.075 under the same conditions as ethylbenzene. The chief product of the action is *phenylnitropropane*, $\text{C}_6\text{H}_5\cdot\text{NO}_2$, which boils at 141° under 25 mm. pressure without undergoing decomposition. Its sp. gr. at $20^{\circ}/0^{\circ}$ is 1.0866. It forms soluble alkali salts whose solutions are precipitated by salts of the heavy metals. On treatment with stannous chloride in acid solution, it yields ethyl phenyl ketone and *phenylamidopropane*, $\text{CHEtPh}\cdot\text{NH}_2$; this boils at $204\text{--}206^{\circ}$, and its sp. gr. = 0.9424 at $20^{\circ}/0^{\circ}$.

Pseudocumene, with nitric acid of sp. gr. 1.075 at $105\text{--}110^{\circ}$, gives a mixture of two *xylylnitromethanes*, namely, $\text{C}_6\text{H}_3\text{Me}_2\text{CH}_2\cdot\text{NO}_2$ [1 : 3 : 4] and [1 : 2 : 4].

J. W.

Derivatives of Mesitylene. Hydrolysis of Aromatic Nitriles.

By F. W. KÜSTER and A. STALLBERG (*Annalen*, 278, 207—223).—*Preparation of Mesitylene*—A cold mixture of concentrated sulphuric acid and water (2:1) is gradually added to commercial acetone contained in a reflux apparatus, and, after remaining 24 hours, the mixture is slowly distilled. Unaltered acetone first passes over, and subsequently (between 150° and 200°) crude mesitylene, which is shaken with sodium hydroxide and purified by fractional distillation over sodium; the yield is 13·5 per cent. of the theoretical.

β -Isoduronitrile, $C_6H_2Me_3CN$ [$Me_3:CN = 1:3:5:4$], is obtained from mesidine by Sandmeyer's method together with a little mesitol. The authors find that mesitol melts at 70—71°; β -isoduronitrile at 55°. The latter cannot be converted into the carboxylic acid either by heating it with acids or alkalis, and it is noteworthy that tetramethylbenzonitrile (Abstr., 1884, 1320) and pentamethylbenzonitrile (Abstr., 1893, 1128) are similarly indifferent. In each of these compounds, the hydrogen atoms contiguous to the cyano-group are replaced by methyl. The experiments to be described were made to ascertain the behaviour of derivatives of β -isoduronitrile in which negative radicles are substituted for the hydrogen atoms.

Nitro- β -isoduronitrile, $NO_2 \cdot C_6HMe_3 \cdot CN$, is obtained by nitrating β -isoduronitrile, but, more conveniently from dinitromesitylene (Fittig, *Annalen*, 141, 133). The dinitromesitylene is heated with alcoholic ammonium sulphide in an autoclave at 100° for 20 hours, and the resulting nitramidomesitylene converted into *nitro- β -isoduronitrile* by Sandmeyer's method; this boils at 277·5° (750 mm.), and melts at 90°. When heated with concentrated hydrochloric acid for six hours at 180—200°, *nitro- β -isodurylic acid*, $NO_2 \cdot C_6HMe_3 \cdot COOH$, is obtained; it melts at 182°. A small quantity of *nitro- β -isoduramide*, $NO_2 \cdot C_6HMe_3 \cdot CO \cdot NH_2$, is also simultaneously produced; in one experiment, the authors obtained a quantitative yield of the amide by boiling the nitrile with dilute sulphuric acid.

Amido- β -isoduronitrile, $NH_2 \cdot C_6HMe_3 \cdot CN$, is obtained when the corresponding nitro-derivative is reduced with stannous chloride; it crystallises in long, delicate needles, melts at 35°, and gives the *dinitrile*, $C_6HMe_3(CN)_2$, by Sandmeyer's method. The latter melts at 142°, and cannot be hydrolysed. *Nitrodicyanomesitylene*, $NO_2 \cdot C_6Me_3(CN)_2$, is formed by warming the last compound with fuming nitric acid; it melts at 118°.

Dinitro- β -isoduronitrile, $CN \cdot C_6Me_3(NO_2)_2$, is obtained by heating the corresponding mononitro-derivative, described above, with a mixture of equal volumes of concentrated sulphuric acid and fuming nitric acid; it forms white needles, melts at 178°, and yields *dinitro- β -isodurylic acid*, $C_6Me_3(NO_2)_2 \cdot COOH$, when heated with concentrated hydrochloric acid at 200—210°; the latter melts at 228°, and its amide melts at 198°. *Nitramido- β -isoduronitrile*, $NO_2 \cdot C_6Me_3(NH_2) \cdot CN$, is prepared by heating the dinitro-compound with alcoholic ammonium sulphide in an autoclave at 100°; it melts at 230°, and yields *nitro-dicyanomesitylene* (m. p. 118°; see above) by Sandmeyer's method.

Amidodicyanomesitylene, $NH_2 \cdot C_6Me_3(CN)_2$, is obtained by reducing

the nitro-compound with stannous chloride; it melts at 135° , and, if treated by Sandmeyer's method, yields the *tricyano*-derivative, $C_6Me_3(CN)_3$, which melts at 165° , and cannot be hydrolysed.

A. R. L.

Orthocyanobenzyllic Cyanide. By S. GABRIEL and T. POSNER (*Ber.*, 27, 827—837).—By the action of sodium ethoxide on "diacetylorthocyanobenzyllic cyanide" (*Abstr.*, 1893, i, 228), a compound is obtained which crystallises from alcohol, melts at 119° , and on treatment with hydriodic acid, is resolved into ethylic iodide and methylcyanisocarbostyryl, the compound is, therefore, *α*-*crthocyno-β*-*ethoxyallylbenzene*, $CN \cdot C_6H_4 \cdot C(CN) : CMe \cdot OEt$, and the formation of methylcyanisocarbostyryl is preceded by that of the hypothetical compound, $CN \cdot C_6H_4 \cdot C(CN) : CMe \cdot OH$. The production of the allylbenzene derivative shows that "diacetylorthocyanobenzyllic cyanide" has the formula $CN \cdot C_6H_4 \cdot C(CN) : CMe \cdot OAc$, and should accordingly be termed *ψ*-*diacetylcyano*benzyllic cyanide.

1:3-Methoxymethylisoquinoline, $C_8H_7 \cdot \begin{matrix} CH \\ (COMe) \cdot N \end{matrix} \begin{matrix} — \\ CMe \end{matrix}$, is prepared by the action of sodium methoxide on chloromethylisoquinoline, it melts at 32° , forming a colourless, viscid liquid, and boils at 258° under a pressure of 764 mm. With acids, it yields salts which are decomposed by water. 1:3-Ethoxymethylisoquinoline is prepared in a similar manner to the methoxy-derivative which it closely resembles; it boils at 266° under 764 mm. pressure.

By the action of benzoic chloride on orthocyanobenzyllic cyanide in presence of potash, *ortho-α*-*dicyano-β*-*hydroxystilbene*,



is formed, and not *benzoylcyanobenzyllic cyanide*, $CN \cdot C_6H_4 \cdot CHBz \cdot CN$, as might be expected; it crystallises from ether in colourless, transparent, needles, and melts at 105 — 106° or 109 — 110° , according to the rapidity of heating; at higher temperatures (110 — 120°) it is converted into a yellow crystalline compound, which melts at 290° . The *silver salt* is yellow and flocculent; the *potassium salt* is crystalline, and on treatment with hydrochloric acid is converted into cyanophenylisocoumarin, which is colourless, and not lemon coloured as previously stated (*loc. cit.*); phenylcyanisocarbostyryl melts at 285° .

By the action of hydrogen chloride on dicyanohydroxystilbene in ethereal solution, a pulverulent, colourless additive compound, $C_{14}H_{11}N_2OCl$ is formed, which softens at 220° and melts at about 270° ; on treatment with hydrochloric acid at 100° , the compound $C_{14}H_{11}N_2O_2Cl$ is obtained in microscopic needles, melting at 196° . *Acetylortho-α*-*dicyano-β*-*hydroxystilbene*, $CN \cdot C_6H_4 \cdot C(CN) : CPh \cdot OAc$, crystallises in needles and melts at 211 — 213° . The *ethoxy derivative*, $CN \cdot C_6H_4 \cdot C(CN) : CPh \cdot OEt$, prepared from the silver or potassium salt, crystallises in transparent prisms, melting at 115 — 116° ; and on treatment with hydriodic acid is resolved into ethylic iodide, ammonia, and cyanophenylisocoumarin. The *methoxy-derivative* crystallises in colourless needles, melting at 140 — 143° .

Ortho-α-*tricyanodibenzyl*, $CN \cdot C_6H_4 \cdot CH(CN) \cdot CH_2 \cdot C_6H_4 \cdot CN$, is pre-

pared by the action of alcoholic potash on a mixture of cyanobenzyllic cyanide and cyanobenzyllic chloride, and is formed in small quantity in the preparation of dicyanohydroxystilbene; it crystallises from alcohol, melts at 114° , and is being further investigated.

By the action of soda on orthocyanobenzyllic cyanide a yellow basic compound is obtained, which is insoluble in ordinary media, but dissolves in dilute acids and in alkalis, but not in ammonia. The hydrochloride, $C_6H_5N_2O.HCl + H_2O$, crystallises in greenish-white, flat needles, and decomposes at $190-200^{\circ}$. The picrate is yellow and crystalline, and melts at $195-205^{\circ}$ with decomposition.

J. B. T.

Ethylphenols. By A. BÉHAL and E. CHOAY (*Compt. rend.*, 118, 422—425).—Three ethylphenols have been described, and the authors have investigated these compounds, using new methods of preparation. The ortho- and para-derivatives were obtained by nitrating ethylbenzene, reducing to amines, and converting the latter into acetyl-derivatives, which were separated by means of the greater solubility of the ortho-derivative in water. The ortho-compound was purified by crystallisation from alcohol, and melts at $111-112^{\circ}$; the para-derivative was crystallised from benzene, and melts at 92° . These amides, when boiled with hydrochloric acid, are rapidly converted into amines, and when the latter are diazotised in dilute sulphuric acid they yield the phenols in a state of purity.

In the preparation of the meta-derivative, the acetyl-derivative of parathyphenylamine was nitrated, boiled with hydrochloric acid to remove the acetyl-group, and then treated with amyllic nitrite in presence of sulphuric acid and absolute alcohol to remove the amide group. The metanitroethylbenzene thus obtained was reduced with iron and acetic acid, and then diazotised in presence of dilute sulphuric acid.

Ortho-ethylphenol boils at $202-203^{\circ}$; sp. gr. at $0^{\circ} = 1.0371$. With ferric chloride, it gives a blue-violet coloration. The benzoate boils at 314° , and crystallises from alcohol in large crystals, which melt at 39° .

Meta-ethylphenol boils at 214° , and separates from methylic chloride in crystals, which melt at -4° . With ferric chloride, it gives a violet coloration. The benzoate crystallises readily from alcohol, melts at 52° , and boils at 322° ; the acetate boils at $222-223^{\circ}$, sp. gr. at $0^{\circ} = 1.0403$.

Parethylphenol melts at $45-46^{\circ}$ and boils at $215-216^{\circ}$; it is slightly soluble in cold water, more soluble in hot water, and very soluble in alcohol, ether, and benzene. With ferric chloride, it gives a blue coloration with a violet tinge. The benzoate boils at 328° , and crystallises from alcohol of 95° in lamellæ, which melt at $59-60^{\circ}$. Parethylphenol is identical with the compound hitherto distinguished as α -ethylphenol.

C. H. B.

Constitution of Orcinol. By DE FORCRAND (*Compt. rend.*, 118, 421—422).—The thermal value of the first function of orcinol is $+40.23$ Cal., and of the second function 39.13 Cal., the mean value

being 39.68 Cal. The difference between the two values is smaller than in the case of the para-phenols, and much smaller than in the case of ortho-phenols. It follows that in orcinol the hydroxyl groups are in the meta position as in resorcinol. The excess of acidity seems to be due to the first function, since the thermal value of the second function is practically identical with that of ordinary phenol.

C. H. B.

Action of Aldehydes on Nitroso-derivatives. By J. PINNOW and G. PISTOR (*Ber.*, **27**, 602—609; compare *Abstr.*, 1893, i, 509).—Methylic iodide forms no additive product with 1:4-formylamidodimethylaniline, $\text{CHO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$; the formyl group is eliminated, and penta- or tri-methylphenylenediamine iodide formed, according to circumstances. Nitrous acid converts it into 1:3:4-nitroformylamidodimethylaniline, $\text{CHO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3\cdot\text{NMe}_2$, which crystallises in lustrous red needles melting at 86° , and can be transformed by reduction with tin and hydrochloric acid into the already known 1:3:4-dimethyltriamidobenzene, $\text{C}_6\text{H}_3(\text{NH}_2)_3\cdot\text{NMe}_2$. This base yields an acetyl derivative when mixed with acetic anhydride; if the mixture is heated, methylic acetate is formed (showing that a methyl group has been removed) together with methylethenylacetylamidophenyleneamidine, $\text{NHAc}\cdot\text{C}_6\text{H}_3\langle\text{NMe}\rangle\text{N}\text{CMe} + \text{H}_2\text{O}$, which crystallises in plates, melts when anhydrous at 238.5° , yields a *picrate*, with $1\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, melting at 226° , and, when boiled with hydrochloric acid, loses the acetyl-group, yielding the base itself, which crystallises in white plates, stable in air, and melting at 76° . Pure para-formaldehyde yields the same products with nitrosodimethylaniline as does the 40 per cent. solution of formaldehyde, only the action is more violent, and more resinous products are formed. Formaldehyde has also some reducing action on nitrosodimethylamine, in which the nitroso-group is joined to nitrogen instead of to carbon; no definite compounds could, however, be isolated from the product.

Acetaldehyde has no action on nitrosodimethylaniline. Formaldehyde is thus the only aldehyde that is capable of reducing the nitroso- to the amido-group.

C. F. B.

Reactions of Orthotolidine. By H. SCHIFF and A. OSTROGOVICH (*Annalen*, **278**, 375—379, and *Gazzetta*, **24**, i, 56—60; compare this vol., i, 236).—*Orthotolidine hydrochloride*, $\text{C}_{10}\text{H}_{10}\text{N}_2\cdot\text{HCl}$, is obtained by boiling the dihydrochloride with sodium acetate in aqueous solution. It crystallises in lustrous, colourless scales, which decompose at above 300° , and soon redden on exposure to the air; even in small quantities it provokes violent sneezing. It is readily soluble in hydrochloric acid yielding the dihydrochloride; the monhydrochloride is recommended as a source for obtaining pure salts of orthotolidine. The monhydrochloride yields diacetylolidine when heated with acetic anhydride or glacial acetic acid; with potassium cyanate, carbonic anhydride and tolidine are formed, and on treatment with ethylic chlorocarbonate the dihydrochloride and tolidindimethane melting at 190 — 190.5° are obtained.

The dihydrochloride is soluble in 17.34 parts of water at 12°, and the monhydrochloride in 112.4 parts. W. J. P.

Aromatic Diazo-compounds and Nitrosamines. By H. v. PECHMANN and L. FROBENIUS (*Ber.*, 27, 651—658; compare *Abstr.*, 1893, i, 154).—The authors have already shown that by the action of benzoic chloride on alkaline solutions of diazo-compounds a benzoylated nitrosamine is formed. Acetic anhydride acts in a similar way, and yields acetylated nitrosamines; these are identical with the compounds obtained by the action of nitrous acid on acid anilides.

Benzoylparatolylnitrosamine, C_7H_7NBzNO , is obtained by shaking an alkaline solution of diazotoluene containing sodium acetate with benzoic chloride. It crystallises in pale, yellow needles, explodes at 74—75°, decomposes on exposure to air or in a closed vessel, and decomposes in solution yielding benzotoluidide and nitrous acid. When reduced with zinc dust and acetic acid, it yields benzotoluidide.

Benzoylphenylnitrosamine crystallises in yellow needles and explodes at 75—76°.

Acetylparatolylnitrosamine, C_7H_7NAcNO , obtained from diazotoluene and acetic anhydride, melts at 80°, and has the properties assigned to it by O. Fischer, who prepared it by the action of nitrous acid on acetoluidide.

Thus aromatic amines, when treated with nitrous acid and then with acetic anhydride, or *vice versa*, yield the same compounds; whence the authors conclude that diazobenzene and acetanilide have analogous constitutions, that is that diazobenzene is the anilide of nitrous acid. In accordance with this view is the production of nitrous acid when an alkaline solution of diazobenzene is gradually added to a boiling concentrated solution of sodium hydroxide.

When diphenylnitrosamine and paratoluidine, dissolved in light petroleum, are left for about a week, diazoamidotoluene is formed; a reaction which the authors explain by supposing that the nitrosamine loses its nitroso-group, which then diazotises the toluidine. Nitroso-anilides react easily with amido-compounds, and thus show a similarity to diazobenzene. Nitroso-acetanilide and toluidine yield diazoamidobenzenetoluene when mixed in molecular proportion; if an excess of base is present, then diazoamidotoluene is obtained. Acetylparatolylnitrosamine and aniline also yield diazoamidobenzenetoluene. Nitrosoanilides also react with phenols, and acetylparatolylnitrosamine and resorcinol yield paratoluenediazoresorcinol.

E. C. R.

Paranitrodiazobenzene. By H. v. PECHMANN and L. FROBENIUS (*Ber.*, 27, 672—673).—The sodium salt of paranitrodiazobenzene, $NO_2C_6H_4NNaNO$, recently described by Schraube and Schmidt (this vol., i, 237), has been prepared independently by the authors; its constitution is shown by the production of a highly unstable crystalline compound with aniline, which is being further investigated. With methylic iodide, paranitrophenylnitrosamine, $NO_2C_6H_4NMeNO$, is formed. *Silver paranitrodiazobenzene*, $NO_2C_6H_4NNOAg$, is obtained

from the sodium salt by the action of silver nitrate, and on treatment with methylic iodide yields *paranitrodiazobenzene methyl ether*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{N:NOMe}$, which crystallises in almost colourless needles, and melts at 83° . On boiling with dilute acids, nitrogen is evolved, and *paranitrophenol* is formed. By the action of aniline in alcoholic solution, *paranitrodiazoamidobenzene*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{N:N:NHPH}$, is obtained, whilst, on treatment with phenol *paranitrobenzeneazophenol*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is formed the *acetyl-derivative* of which crystallises in flesh-coloured needles, and melts at 146° . J. B. T.

Aromatic Bisdiazo Compounds. By H. v. PECHMANN and L. FROBENIUS (*Ber.*, 27, 703—706; compare *Ber.*, 27, 651, preceding abstracts)—Nitrosoacetanilide, or nitrosobenzanilide, reacts with aniline in the presence of free alkali to form *bisdiazobenzeneanilide* (benzenediazoanilinediazobenzene), NPh(N:NPh)_2 . The same compound may be obtained by treating aniline dissolved in methylic alcohol with a solution of diazobenzene chloride in the same solvent in the presence of sodium methoxide, at a low temperature. It forms yellow, lustrous plates, and is sparingly soluble in ether and alcohol, readily in benzene and chloroform. When heated to $80\text{--}81^\circ$, it explodes with a loud report, and also explodes when struck. Its constitution is shown by the fact that, when boiled with a mineral acid, it decomposes quantitatively, according to the equation $\text{NPh(N:NPh)}_2 + 2\text{H}_2\text{O} = 2\text{PhOH} + 2\text{N}_2 + \text{NH}_2\text{Ph}$. The compound can be preserved without alteration.

Bisparadiazotolueneparatoluidide, $\text{C}_6\text{H}_4\text{N(N:N}\cdot\text{C}_6\text{H}_4)_2$, may be obtained from nitrosoacetotoluidide or nitrosobenzotoluidide; by the direct action of diazoparatoluene chloride on *paradiazoaamidotoluene* in alcoholic solution; or by the action of diazotoluene chloride on *toluidine*. It forms sulphur yellow needles, and is sparingly soluble in ether, readily in benzene and chloroform. It explodes when vigorously struck, or when heated, but less violently than the aniline compound. It may be heated in a melting point tube to 86° , and then detonates gently. It is decomposed by acids in a similar manner to the aniline compound. A. H.

Benzenediazoic Acid from Nitryl Chloride and Aniline. By E. BAMBERGER (*Ber.*, 27, 668—671).—Having obtained benzenediazoic acid from nitric anhydride and aniline (this vol., i, 239), the author has attempted to prepare it from nitryl chloride and aniline, the results confirm the doubts as to the existence of nitryl chloride expressed by others; in any case it is not obtained pure by any of the methods described below. Benzenediazoic acid is not formed by the action of nitric oxide, nitrous anhydride, nitric acid, or nitrosyl chloride on aniline. "Nitryl chloride," prepared by Williamson's method from chlorosulphuric acid and potassium nitrate, was obtained as a colourless gas, and was allowed to act on aniline in ethereal solution at low temperatures, the yield of benzenediazoic acid was 0.3 gram from 41 grams of aniline; the following substances were also formed: diazoamidobenzene, orthonitraniline, azobenzene, and probably *paranitraniline*, and diazobenzene salts. The "nitrylic

chloride" formed by Exner's method from silver nitrate and phosphorus oxychloride is a reddish-brown gas; with aniline (50 grams) it yields benzenediazoic acid (0.05 gram), diazoamidobenzene, and possibly traces of orthonitraniline and paranitraniline. Hasenbach's "nitrylic chloride" from nitrogen peroxide and chlorine appears to consist chiefly of nitrosyl chloride, as, on treatment with aniline, it yields diazoamidobenzene, aniline nitrate and hydrochloride, azobenzene, diazobenzene nitrate and hydrochloride, and possibly orthonitraniline. Benzenediazoic acid could not be detected with certainty. Aniline hydrochloride, diazobenzene chloride, and diazoamidobenzene are the sole products formed by the action of nitrosyl chloride on aniline. Nitric peroxide or nitric acid (b. p. 86°) and aniline yield aniline nitrate, diazobenzene nitrate, diazoamidobenzene, and in small quantity ortho- and para-nitraniline. With nitrous anhydride, the products were the same, with the exception of ortho- and para-nitraniline. Nitric acid and nitrous anhydride both appear to yield traces of benzenediazoic acid.

J. B. T.

Tertiary and Quaternary Aromatic Hydrazines. By C. D. HARRIES (*Ber.*, 27, 696—702).—Tertiary hydrazines can be prepared from the formyl-derivatives of the secondary hydrazines, but not from the acetyl-derivatives, because the acetyl-group cannot be removed without the decomposition of the molecule.

Phenylmethylformylhydrazine, $\text{NMe}\cdot\text{Ph}\cdot\text{NH}\cdot\text{CHO}$, forms a white crystalline mass melting at $50-51^{\circ}$. It has a not unpleasant smell, boils at $183-185^{\circ}$ under a pressure of 11 mm., and is soluble in alcohol, but scarcely in water.

Phenyldimethylformylhydrazine, obtained by the action of methylic iodide on the sodium compound of this formyl-derivative, is a colourless liquid; it boils at $147-148^{\circ}$ (7 mm.), and is very sparingly soluble in dilute acids.

Phenyldimethylhydrazine, $\text{NMePh}\cdot\text{NHMe}$, is a bright green, highly-refractive liquid, which boils at $93-94^{\circ}$ (7 mm.). It reduces silver nitrate solution in the cold, but scarcely acts on Fehling's solution even on boiling. It is very soluble in all solvents except water, and gives a rose-red coloration with bleaching powder solution. The *hydrobromide* and *hydriodide* crystallise well, whilst the *hydrochloride* and *sulphate* are very soluble. The *ferrocyanide* crystallises in rhombic tablets, and is employed in the purification of the base.

Phenyldimethylnitrosohydrazine, obtained by the action of sodium nitrate on a solution of the base in hydrochloric acid, is a dark red, thick oil, which gives Liebermann's reaction; it decomposes when distilled in a vacuum, the base being largely regenerated. The nitroso-compound is scarcely attacked by continued boiling with aqueous soda, and does not undergo intramolecular change when treated with alcoholic hydrochloric acid. On reduction, it yields methylaniline and methylhydrazine.

Phenyldimethylbenzoylhydrazine crystallises from alcohol in large, feathery plates melting at $103-104^{\circ}$.

Phenyltrimethylhydrazine, $\text{NMePh}\cdot\text{NMe}_2$, is obtained by the action of methylic iodide on phenyldimethylhydrazine. It forms a colour-

less oil, which boils at 93—94° (8 mm.), and has a characteristic odour of cedar wood. It gives no coloration with bleaching powder, does not reduce Fehling's solution at all on boiling, but reduces silver solution in the cold. The base easily decomposes with formation of dimethylaniline, and probably dimethylamine. The only salt which has been obtained in the solid state is the *ferrocyanide*.

Phenyldimethylmethyazonium iodide, $\text{NMe}_2\text{PhI}\cdot\text{NHMe}$, is readily soluble in water, and forms thin plates melting at 145°, after becoming brown at 80°.

Phenylmethylethylformylhydrazine boils at 169° (12 mm.), and is a colourless oil. *Phenylmethylethylhydrazine* boils at 101—102° (9 mm.). The *hydrobromide* forms large, blunted prisms. The *nitroso-compound* is a thick, dark red oil, which on reduction yields methylhydrazine and ethylhydrazine.

A. H.

Acid Imides and Hydrazine Hydrate. By R. v. ROTHENBURG (*Ber.*, 27, 691—692).—*Amidophthalimide*, $\text{CO} < \text{O} > \text{C:N}\cdot\text{NH}_2$, is prepared by heating phthalimide with hydrazine hydrate or acetate in alcoholic solution; it is a colourless, sparingly soluble powder, melting at 250—251°.

Benzalamidophthalimide, $\text{CO} < \text{O} > \text{C:N}\cdot\text{N:CHPh}$, is formed by the action of benzaldehyde on the preceding compound in aqueous solution at the ordinary temperature; it is almost completely insoluble, remains unchanged at 250°, and is resolved into its constituents on treatment with acids or alkalis.

Isopropyleneamidophthalimide, $\text{CO} < \text{O} > \text{C:N}\cdot\text{N:CMe}_2$, is obtained by heating amidophthalimide with acetone; it melts at 260°, and is sparingly soluble. Hydrazine derivatives of succinimide could not be prepared; this, in the author's opinion, points to the formula, $\text{CO} < \text{O} > \text{C:NH}$ for phthalimide, whilst succinimide is probably symmetrical.

J. B. T.

Oxindophenolic Colouring Matters from Gallanilide and Galloparatoluidide. By P. CAZENEUVE (*Bull. Soc. Chim.*, [3], 11, 85—87).—The colouring matters from gallanilide have been already described (*Abstr.*, 1893, i, 510). Those from its homologue are exactly analogous, and in physical respects almost identical.

JN. W.

Diacid Anilides. By G. TASSINARI (*Gazzetta*, 24, i, 61—62).—The author was endeavouring to prepare diacid anilides when he was anticipated by Kay (this vol., i, 76), whose results he confirms.

On heating a mixture of formanilide, acetic anhydride, and sodium acetate, a crystalline product is ultimately obtained, which could not be freed from acetanilide; for this reason, possibly, the analytical results do not agree with those of formacetanilide.

Diacetanilide may be prepared by treating acetanilide with acetic anhydride; it is instantly decomposed by aqueous ammonia, giving

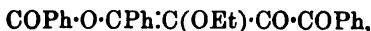
acetanilide and ammonium acetate, whilst on treatment with ammonia dissolved in anhydrous ether, it yields acetamide and acetanilide. It is also conveniently prepared by the action of acetic chloride on sodioacetanilide, using benzene as a diluent; when heated at 40° with decinormal soda solution, one acetyl group is removed quantitatively.

Parabromodiacetanilide forms small crystals melting at 69—70°; it behaves similarly to diacetanilide with decinormal soda, and with aqueous and dry ammonia. W. J. P.

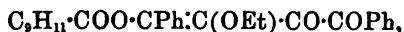
The Formoins. By W. ABENIUS (*Ber.*, 27, 706—719).—Benzoylformoin, when treated in alcoholic solution with hydroxylamine hydrochloride, yields, in addition to other products, a substance of the formula $C_{18}H_{16}O_4$ (Abstr., 1892, 69). This compound is *β-ethylbenzoylformoin*, $OH \cdot CPh \cdot C(OEt) \cdot CO \cdot CPh$, and is quantitatively formed by the action of hydrogen chloride on an alcoholic solution of benzoylformoin; with alkalis it gives yellow salts, which are soluble in dilute, but not readily in concentrated, aqueous alkalis. Nitric acid converts it into diphenyltetraketone. When it is boiled with acetic anhydride, *acetyl-β-ethylbenzoylformoin*,



is formed; this crystallises from alcohol in groups of short, colourless prisms melting at 121—122°, and is readily hydrolysed by aqueous potash or by the addition of strong hydrochloric acid to its alcoholic solution, the *β-ethyl* compound being quantitatively regenerated. *Benzoyl-β-ethylbenzoylformoin*,

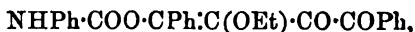


separates from alcohol in aggregates of small, white crystals melting at 147°, and is very readily hydrolysed. The *paratoluylderivative*, $C_7H_7 \cdot COO \cdot CPh \cdot C(OEt) \cdot CO \cdot CPh$, forms long, colourless crystals, which dissolve readily in alcohol, benzene, and ether, and melt at 125—126°. On hydrolysis, it is quantitatively converted into ethylbenzoylformoin. The *cuminoylderivative*,



forms short prisms melting at 108—109°; it is only slightly soluble in cold alcohol. On hydrolysis, it is, like the other derivatives, quantitatively converted into ethylbenzoylformoin.

The fact that all these acid derivatives of *β-ethylbenzoylformoin* are converted by hydrolysis into ethylbenzoylformoin seems to show that they are derived from the dihydroxyl form of benzoylformoin, $OH \cdot CPh \cdot C(OH) \cdot CO \cdot CPh$, and not from the alcoholic form, $CPh \cdot CH(OH) \cdot CO \cdot CPh$. This view is confirmed by the reactions of the other derivatives containing two acid or alkyl groups, and by the fact that ethylbenzoylformoin itself combines with phenylcarbimide to form a crystalline *additive product*,



which forms nacreous plates melting at 159—160°.

β-Methylbenzoylformoin, $OH \cdot CPh \cdot C(OMe) \cdot CO \cdot CPh$, is prepared in

a similar manner to the ethyl derivative, and is readily soluble in alcohol, ether, &c. It resembles the ethyl compound in its reactions. The *acetyl-derivative*, $\text{OAc}\cdot\text{CPh}\cdot\text{C}(\text{OMe})\cdot\text{CO}\cdot\text{COPh}$, crystallises in short, lustrous, colourless prisms melting at 95° . The *cuminoyl-derivative*, $\text{C}_9\text{H}_{11}\cdot\text{COO}\cdot\text{CPh}\cdot\text{C}(\text{OMe})\cdot\text{CO}\cdot\text{COPh}$, forms spherical aggregates of short prisms, and melts at 112° .

β -*Amylbenzoylformoin* is prepared in a similar manner, and is readily soluble in alcohol. β -*Benzylbenzoylformoin* crystallises from alcohol in yellow needles melting at $182\text{--}183^\circ$. β -*Ethylparatoluy-formoin*, $\text{C}_7\text{H}_7\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OEt})\cdot\text{CO}\cdot\text{COPh}$, is formed when an alcoholic solution of paratoluyformoin is saturated with hydrogen chloride; it crystallises from light petroleum in thin plates melting at $140\text{--}146^\circ$. The *benzoyl derivative*, $\text{C}_7\text{H}_7\cdot\text{C}(\text{O}\cdot\text{COPh})\cdot\text{C}(\text{OEt})\cdot\text{CO}\cdot\text{COPh}$, is amorphous, and, on hydrolysis, yields benzoic acid and β -ethylparatoluy-formoin.

$\alpha\beta$ -*Diethylbenzoylformoin*, $\text{OEt}\cdot\text{CPh}\cdot\text{C}(\text{OEt})\cdot\text{CO}\cdot\text{COPh}$, is prepared by boiling an alcoholic solution of β -ethylbenzoylformoin with sodium ethoxide and ethylic iodide. It separates from hot alcohol in lustrous crystals melting at $83\text{--}84^\circ$. It is perfectly neutral to dilute alkalis and acids, and is converted by nitric acid into a resin.

α -*Ethylbenzoylformoin*, $\text{OEt}\cdot\text{CPh}\cdot\text{C}(\text{OH})\cdot\text{CO}\cdot\text{COPh}$, is formed by the action of concentrated sulphuric acid on the foregoing compound; it crystallises from alcohol in short, yellow, monosymmetric prisms melting at $137\text{--}138^\circ$, is readily soluble in dilute alkalis, and is converted by nitric acid into a resinous mass. When its solution in alcohol is saturated with hydrogen chloride, it is reconverted into diethylbenzoylformoin. The *acetyl derivative*,



is formed by the action of acetic anhydride on the α -ethyl compound, together with another substance which has not been further examined. It crystallises from alcohol in colourless prisms melting at $114\text{--}115^\circ$.

α -*Methyl- β -ethylbenzoylformoin*, $\text{OMe}\cdot\text{CPh}\cdot\text{C}(\text{OEt})\cdot\text{CO}\cdot\text{COPh}$, is prepared by boiling β -ethylbenzoylformoin in alcoholic solution with sodium methoxide and methylic iodide; it separates from alcohol in small, crystalline groups, and melts at 105° . It is converted by concentrated sulphuric acid into α -methylbenzoylformoin, which has not yet been further examined.

Diacetylbenzoylformoin, $\text{OAc}\cdot\text{CPh}\cdot\text{C}(\text{OAc})\cdot\text{CO}\cdot\text{COPh}$, is obtained by boiling benzoylformoin with acetic anhydride; it crystallises from alcohol in rosettes of small plates melting at 158° , and is readily converted by hydrolysis into acetic acid and benzoylformoin.

A substance isomeric with this diacetyl-derivative seems to be formed at the same time; it melts at $124\text{--}125^\circ$, but was obtained in such small quantity that it could not be examined.

The *bromo-derivative*, $\text{OEt}\cdot\text{CPhBr}\cdot\text{CO}\cdot\text{COPh}$, is formed by treating with bromine diethyl- or α -ethyl-benzoylformoin suspended in water. A red oil is formed, which is probably an additive product containing 2 atoms of bromine, but this soon solidifies, the same compound being finally formed in both cases. It crystallises from a mixture of benzene and light petroleum in light yellow,

lustrous tablets or prisms melting at 101—102°. It is not soluble in alkalis, but is decomposed if boiled with them. It seems probable that an additive compound is first formed, and that then the elements of ethylic bromide or hydrogen bromide are eliminated, the final product being the same in both cases.

Notwithstanding these reactions, which point to the dihydroxyl formula for benzoylformoin, its formation from phenylglyoxal, $\text{C}_6\text{H}_5\text{CHO}$, by condensation in the presence of alcoholic potassium cyanide, and the production of tetraketone derivatives from it by oxidation, seem to indicate that the free compound only contains one hydroxyl group, the dihydroxyl formula being that of a tautomeric form. A. H.

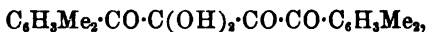
Aromatic Tetraketones. By H. G. SÖDERBAUM (*Ber.*, 27, 658—663; compare *Abstr.*, 1893, i, 169).—1 : 2 : 4-*Xyloylformoxime*,



is obtained by mixing 1 : 2 : 4-xylyl methyl ketone, sodium, amylic nitrite, and alcohol, and, after the action has taken place, dissolving the sodium salt thus formed in ice cold water, and precipitating with acetic acid; it crystallises in short prisms or thick plates, and melts at 121°. The *acetyl compound*, $\text{C}_6\text{H}_5\text{Me}_2\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{NAc}\cdot\text{OH}$, is obtained by treating it with acetic chloride, and, after drying on a porous plate the hydrochloride thus formed, decomposing it with ice cold water. It crystallises in long, white needles, and melts at 130—131°.

1 : 2 : 4-*Xyloylformoin*, $\text{C}_6\text{H}_5\text{Me}_2\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_5\text{Me}_2$, is obtained by treating the above acetyl compound, dissolved in alcohol, with potassium cyanide. It is a crystalline, sulphur-yellow substance, sinters at 138°, and melts at 146°. It cannot be recrystallised without decomposition, and, when dissolved in benzene, decomposes into two acid compounds melting at 92° and 163—164°, which are probably orthoxylylgyoxylic acid and metaparadimethylbenzoic acid respectively.

1 : 2 : 4-*Dirylyltetraketone monhydrate*,



is obtained by treating the above formoin with nitric acid. It crystallises in short, yellow prisms, sinters at 103°, melts at 108° with decomposition, and gradually decomposes when allowed to remain in a desiccator.

1 : 4 : 2-*Xyloylformoxime*, $[\text{Me}_2 : (\text{CO}\cdot\text{CH}\cdot\text{NOH}) = 1 : 4 : 2]$, obtained, together with isoxylylic acid, in the same way as the 1 : 2 : 4-compound, crystallises in beautiful, pale yellow needles, and melts at 63°. The *acetyl-compound* crystallises in hard, white nodules, melts at 135—136°, and, when dissolved in alcohol, gives an intense red coloration with ferric chloride.

1 : 4 : 2-*Xyloylformoin* crystallises in microscopic prisms, sinters at 160°, melts at 164—168°, and decomposes, when allowed to remain in contact with its solvents, yielding a compound which melts at 125—130°, probably isoxylylic acid.

1 : 4 : 2-*Dirylyltetraketone monhydrate* crystallises in beautiful, bright

yellow prisms, reddens at 100° , softens at 105° , and melts at $109-110^{\circ}$ with decomposition.

The dixylyltetraketones of the ortho- and para-series, like the corresponding phenyl, tolyl, and bromophenyl compounds, yield monohydrates, whereas dimetaxylyltetraketone exists either in the unhydrated form or yields a dihydrate. E. C. R.

Isomerism of Nitrobenzoic acids. By O. DE CONINCK (*Compt. rend.*, 118, 471—473).—The nitrobenzoic acids, like the amidobenzoic acids, can be groups in pairs according to their solubilities in different solvents. In water and dilute alcohol, the ortho- and meta-acids are easily soluble; the para-acid is only slightly soluble. In ether, the order is the same, but in all three cases the numerical values are much higher. With chloroform and benzene, the para-derivative is very slightly soluble, the meta-derivative is easily soluble, whilst the ortho-derivative shows intermediate solubility. In carbon bisulphide and light petroleum, the meta-acid is the most soluble, whilst the ortho- and para-acids are much less soluble.

C. H. B.

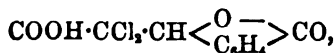
Guaiacolglycollic acid. By A. CUTOLO (*Gazzetta*, 24, i, 63—64).—*Guaiacolglycollic acid*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$, is prepared by heating guaiacol with monochloroacetic acid on the water bath, and subsequently adding soda and acidifying. It forms beautiful, white needles melting at 120° , and is soluble in alcohol and in water. The *barium* salt crystallises in small, prismatic needles containing $3\text{H}_2\text{O}$, and is very soluble in water. The *silver* salt is obtained in beautiful needles, which become red on exposure to light. W. J. P.

Synthesis of the Cresolcoumarins. By A. CURATOLO and G. PERSIO (*Gazzetta*, 24, i, 45—48).—On heating the sodium cresolglycollates with salicylaldehyde and acetic anhydride, for six hours at $150-160^{\circ}$, condensation occurs, and the corresponding cresolcoumarins are formed. The product is extracted with boiling water and sodium carbonate solution, and the residue purified by dissolving in potash, and precipitating with hydrochloric acid.

Orthocresolcoumarin, $\text{C}_6\text{H}_4\cdot\text{CH}(\text{CO})\cdot\text{C}_6\text{H}_4\cdot\text{Me}$, which crystallises in lustrous, micaceous scales melting at $100-101^{\circ}$, is very soluble in alcohol or ether.

Meta- and *para-cresolcoumarin* resemble the ortho-isomeride in appearance and behaviour towards solvents; they melt at $106-107^{\circ}$ and $113-114^{\circ}$ respectively. All three isomerides yield coumaric acid on prolonged boiling with 50 per cent. potash. W. J. P.

Action of Bleaching Powder and Hypochlorous acid on Quinones.—By T. ZINCKE and W. SCHMIDT (*Ber.*, 27, 733—744; compare *Abstr.*, 1892, 1229—1232).—The lactone of α -dichloro- β -hydroxyorthohydrocinnamocarboxylic acid,



is obtained by the action of bleaching powder solution on monochloro- β -naphthaquinone. It crystallises in small, fine, prismatic needles melting at 157° , is insoluble in light petroleum, and crystallises from hot water in tablets containing $1\text{H}_2\text{O}$. The *sodium salt*, $\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4\text{Na}$, forms crystalline granules. The *methylic salt* separates from a mixture of ether and light petroleum in large, colourless crystals, melting at 77° . The lactone, by reduction, is converted into ortho-hydrocinnamocarboxylic acid. The lactone of α -chlorobromo- β -hydroxyortho-hydrocinnamocarboxylic acid, $\text{COOH}\cdot\text{CClBr}\cdot\text{CH}<\overset{\text{O}}{\text{C}_6\text{H}_4}>\text{CO}$,

is prepared like the dichloro-compound by the action of bleaching powder on monobromo- β -naphthaquinone; it forms colourless, prismatic needles, melts at 175° , and is less soluble than the dichloro-compound.

The dichloro-lactone is accompanied by a monochlorophthalic acid melting at 158° , the constitution of which has not yet been ascertained.

The two lactones just described are converted by the action of aqueous soda or baryta into the lactone of α -keto- β -hydroxyortho-hydrocinnamocarboxylic acid, $\text{COOH}\cdot\text{CO}\cdot\text{CH}<\overset{\text{O}}{\text{C}_6\text{H}_4}>\text{CO}$; this crystallises in fascicular groups of fine needles and melts and decomposes at 246° . It is sparingly soluble in benzene, but readily in alcohol or hot water, and dissolves in alkalis with formation of the salts of the bibasic acid. The *barium salt*, $\overset{\text{C}_6\text{H}_4}{\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{COO}}>\text{Ba} + \text{H}_2\text{O}$, is a yellow crystalline precipitate, which yields the lactone when decomposed by acids. The *oxime*, $\text{C}_{10}\text{H}_7(\text{N}\cdot\text{OH})\text{O}_4$, forms small, colourless prisms, melting at 167 — 168° .

When the above lactone is dissolved in sodium carbonate and treated with sodium hypochlorite, it is converted into the lactone of ortho-hydroxyhomophthalic acid, $\text{COOH}\cdot\text{CH}<\overset{\text{O}}{\text{C}_6\text{H}_4}>\text{CO}$; the latter may also be obtained in a similar manner from isocoumarincarboxylic acid. It crystallises in silky plates, is readily soluble in water and alcohol, and melts at 151 — 152° . The *methylic salt* forms rosettes of broad needles, melting at 54 — 55° . On reduction, the lactonic acid is converted into homophthalic acid.

Dichloro- β -naphthaquinone is converted by bleaching powder into dichloroketohydroxyhydrindenecarboxylic acid, dichlorodiketohydrindene and trichloroacetophenonecarboxylic acid, very little of the first named product being formed if excess of bleaching powder be employed.

The formulæ given above are the most probable, but they have not been proved with certainty. The action of bleaching powder on the chloro- and bromo-derivatives of β -naphthaquinone resembles that of the same reagent on nitronaphthaquinone and differs entirely from its action on β -naphthaquinone itself.

A. H.

Derivatives of Benzenesulphonamide and Hydrazine. By O. HINSBERG (*Ber.*, **27**, 598—602).—When benzenesulphonamide is suspended in water, and treated with sodium nitrite and excess of

sulphuric acid, part is converted into dibenzenesulphonehydroxylamine, $(C_6H_5 \cdot SO_2)_2NOH$; (König's dibenzsulphhydroxamic acid), and part into benzenesulphonic acid, whilst some remains unchanged. If benzenesulphonamide is dissolved in the equivalent amount of aqueous soda, excess of sodium carbonate first added, and then, to the cooled solution, a hydrochloric acid solution of diazobenzene chloride, *benzenesulphonediazobenzeneamide*, $C_6H_5 \cdot SO_2 \cdot NH \cdot N_2 \cdot Ph$, separates in yellow needles; it melts and decomposes at 102° . It is decomposed when warmed with dilute acids or alkalis, the products including benzenesulphonamide, phenol, and nitrogen; it also yields a bromine additive compound.

Benzenesulphonehydrazine cannot be obtained by reducing benzenesulphenonitramide, $C_6H_5 \cdot SO_2 \cdot NH \cdot NO_2$, by any of the usual methods; these yield the sulphonamide instead. Its *benzal derivative*, $C_6H_5 \cdot SO_2 \cdot NH \cdot N \cdot CHPh$, can, however, be obtained in small quantity by mixing the potassium salt of benzenesulphenonitramide with an equal weight of zinc dust, suspending the mixture in water, and, after the lapse of half an hour, adding gradually about half the weight of acetic acid to the cooled solution, filtering, acidifying with hydrochloric acid, filtering again after a time, and finally shaking with benzaldehyde. This derivative forms a yellow crystalline precipitate, and melts at 110° ; it was not found possible to isolate the hydrazine from it, as acids decompose it with liberation of benzaldehyde and phenyl mercaptan; the other products formed, besides the hydrazine, are the sulphonamide, sulphinic acid, and sulphonehydroxylamine. *Dibenzenesulphonehydrazine*, $(C_6H_5 \cdot SO_2)_2N \cdot NH_2$, may be obtained by dissolving hydrazine sulphate in a little water, cooling the solution and then adding excess of potash and benzenesulphochloride; it forms white needles, and melts with decomposition at 245° . It yields a potassium salt which is only sparingly soluble in aqueous potash, and which decomposes when heated into nitrogen and benzenesulphonic acid.

C. F. B.

Action of Benzenesulphonic acid on Potassium Iodide.
New Class of Organic Periodides. By J. H. KASTLE and H. H. HILL (*Amer. Chem. J.*, 16, 116—122).—While studying the action of benzenesulphonic acid on potassium iodide, these substances were heated together in molecular proportion for some time in aqueous solution. The solution became deep red-brown, and after two months was found to contain a large quantity of opaque-green crystals of metallic lustre. These crystals dissolved readily in water, and, on boiling the solution, it was decolorised, large quantities of iodine being evolved. Analysis led to the probable formula $(C_6H_5 \cdot SO_3K)_2KI_5$. This substance is best produced by mixing a strong aqueous solution of potassium benzenesulphonate with the required quantity of iodine dissolved in the smallest possible quantity of potassium iodide solution. *Potassium benzenesulphonate periodide* $(C_6H_5 \cdot SO_3K)_2KI_5$, crystallises in opaque, thin, much elongated, rectangular prisms, of a brilliant, greenish-bronze lustre. They rapidly lose iodine, and their surfaces become dulled. Five-sixths of the iodine appears to be very loosely held. *Sodium benzenesulphonate periodide* $(C_6H_5 \cdot SO_3Na)_2KI_5$, crystallises in transparent, thin, much elongated, rectangular prisms, of a brilliant, greenish-bronze lustre. They rapidly lose iodine, and their surfaces become dulled. Five-sixths of the iodine appears to be very loosely held.

sulphonate peroxide, $(C_6H_5 \cdot SO_2Na)_5NaI_4$, obtained in like manner, closely resembles the potassium salt in appearance and behaviour. The iodine is present, however, in smaller proportion, four-fifths being present in a loosely combined state. A similar barium salt, $[(C_6H_5 \cdot SO_2)_2Ba]_5BaI_2I_{10}$, forms fine needles of greenish-bronze lustre.

L. T. T.

Thiosulphonic acids and Sulphinic acids. By H. LIMPRICHT (*Annalen*, 278, 239—260).—*Metanitrobenzenethiosulphonic acid*, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot SH$, is formed as barium salt when barium hydroxide, suspended in water, is thoroughly saturated with hydrogen sulphide, and finely-pulverised nitrobenzenesulphonic chloride added. The solution is evaporated, and the residue treated with 95 per cent. alcohol, the precipitated barium chloride being filtered off, and the filtrate evaporated. The residue is dissolved in water, and the solution, on remaining over concentrated sulphuric acid, yields crystals of the impure barium salt. A solution of the latter is treated (warmed?) with dilute sulphuric acid, the precipitate of barium sulphate and sulphur filtered off, and the filtrate containing nitrobenzenesulphinic acid treated with dilute ammonium sulphide, whereby ammonium nitrobenzenethiosulphonate is formed, from which the pure barium salt is readily obtained; it crystallises with $2\frac{1}{2}H_2O$. The free acid forms white plates, and melts at 164° .

The preparation of metanitrobenzenesulphinic acid, $NO_2 \cdot C_6H_4 \cdot SO_2H$, is best carried out as already described (*Abstr.*, 1892, 475; 1893, i, 168); a small quantity of metamidobenzenesulphonic acid is simultaneously formed. The pure nitro-acid melts at 98° , and gives a deep-blue coloration with sulphuric acid on addition of a drop of phenol. The *potassium* salt is anhydrous, the *sodium* salt crystallises with $2H_2O$, the *barium* salt with 4 and with $1H_2O$, and the silver salt is so sparingly soluble in water that it is available for the purification and detection of the acid. The *sulphobromide* melts at 68° , and the *anilide* at 122° . When the *sodium* salt is heated with alcohol and ethylic bromide in a sealed tube at 130° , the compound $NO_2 \cdot C_6H_4 \cdot SO_2Et$ is formed; it melts at 100° . With ethylenic bromide under like circumstances, a compound is obtained melting at 226° ; it is probably the disulphone, $C_6H_4(SO_2 \cdot C_6H_4 \cdot NO_2)_2$ (*Otto, Ber.*, 13, 1275). Nitrobenzenesulphinic acid does not react with phosphoric chloride as stated by Otto (*Annalen*, 141, 374), but under these circumstances nitrophenylic bisulphoxide (see below) is formed. The *hydrazine*, $NO_2 \cdot C_6H_4 \cdot SO_2H \cdot N_2H_3Ph$, melts at 131° .

Phenylnitrobenzenesulphazide, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot N_2H_3Ph$, is obtained by mixing phenylhydrazine and nitrobenzenesulphonic chloride in alcoholic solution; it forms bright yellow needles, melts at 154° , and decomposes into nitrogen, benzene, and nitrobenzenesulphinic acid when warmed with alkalis.

Metamidobenzenethiosulphonic acid, $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot SH$, is obtained by dropping nitrobenzenesulphonic chloride into a concentrated aqueous solution of ammonium hydrosulphide; it crystallises in white prisms, and melts at 167° . When warmed with acids, ferric chloride, or potassium iodide, half the sulphur is precipitated, in the latter

case with the liberation of iodine; the sulphur thus obtained being insoluble in carbon bisulphide. The alkali salts of the acid just described are very soluble in water and alcohol. When a solution of the sodium salt is reduced by sodium amalgam, metamidobenzenesulphonic acid, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, is formed; at 210° it carbonises without melting. The alkali salts are so soluble in water and alcohol that they cannot be obtained in crystals.

Nitrophenylic bisulphoxide, $\text{S}_2\text{O}_2(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, is formed, together with nitrobenzenesulphonic acid, by warming nitrobenzenesulphonic acid with acids; it crystallises in yellowish needles, and melts at 123° . If the bisulphoxide is boiled with alkalis, a salt of nitrobenzenesulphonic acid separates, together with a resinous substance, from which *nitrophenylic bisulphide*, $(\text{NO}_2 \cdot \text{C}_6\text{H}_4)_2\text{S}_2$, may be extracted by boiling alcohol; this forms yellow crystals, melts at 82° , and gives a red coloration with concentrated sulphuric acid and an indigo-blue coloration with anhydrous sulphuric acid.

Amidophenylic bisulphide is prepared by reducing the nitro-compound with ammonium sulphide; its salts do not crystallise well. Amidophenylic bisulphoxide, $\text{S}_2\text{O}_2(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$, is obtained, together with amidobenzenesulphonic acid, by warming amidobenzenesulphonic acid with acids; it was not obtained in the pure state.

In preparing metanitrophenyltolylsulphone, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Me}$ (compare Otto, *Ber.*, 11, 2066), by heating together metanitrobenzenesulphonic chloride, aluminium chloride, and carbon bisulphide, it was noticed that the yield was extremely small, nitrophenylic bisulphoxide and other compounds being produced. The sulphoxide is undoubtedly a secondary product formed by the action of acids on nitrobenzenesulphonic acid, and, in proof that the latter is the first product, it is shown to be produced when nitrobenzenesulphonic chloride, aluminium chloride, and carbon bisulphide are heated together in a reflux apparatus for 24 hours; a compound of nitrobenzenesulphonic acid with aluminium chloride was isolated, for which the formula $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2)_3\text{Al}_2\text{Cl}_2$ is given. The conditions for the preparation of metanitrophenyltolylsulphone, as above, have not been ascertained; the compound melts at 93° , and yields *nitrophenylsulphonebenzoic acid*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, when oxidised with chromic acid; this acid melts at 269° , and its barium salt crystallises with $2\text{H}_2\text{O}$.

A. R. L.

Oxidation of Reduced Indoles. By M. KANN and J. TAFFL (*Ber.*, 27, 826—827).—Dihydro-2'-methylindole and dihydro-3'-methylindole are converted, to the extent of about 50 per cent., into 2'-methylindole and 3'-methylindole (skatole) respectively by distillation with silver sulphate (1 mol. : 2 mol. indole). The oxidation cannot be accomplished by the action of mercuric acetate.

J. B. T.

Two Stereoisomeric Hydrazones of Benzoïn. By A. SMITH and J. H. RANSOM (*Amer. Chem. J.*, 16, 108—117).—By acting on an alcoholic solution of benzoïn with phenylhydrazine (1 mol.) Pickel obtained (*Abstr.*, 1886, 545) benzoïn monophenylhydrazone, $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}$,

melting at 155°. The authors find, however, that if the alcoholic mixture is heated on the water bath for three to four hours, and then allowed to cool, a new isomeric β -hydrazone, melting at 106°, is mixed with the other product. The two substances may be separated from one another by dissolving them in boiling light petroleum, the β -compound separating out first on cooling. The best mode of preparing the two isomerides is, however, to dissolve 20 grams of benzoïn and 10 grams of phenylhydrazine in 200 c.c. of 95 per cent. alcohol, warm the solution for three or four hours on the water bath, and then set it aside for 12 hours. A large crop of crystals of the β -hydrazone will then be formed, and, if the liquid is filtered off and well shaken for a few minutes, it deposits the α -form entirely free from admixture with the β -form. If benzoïn and phenylhydrazine, in molecular proportion, are cautiously heated together without any solvent, a thick oil is produced, consisting almost wholly of the β -form.

Both forms crystallise in small, white needles, which do not change colour on exposure to air or sunlight, the α -form yielding thick, the β -form thin, monoclinic prisms. Both are soluble in warm, light petroleum, more so in warm alcohol, and very soluble in benzene. Both dissolve readily in warm acetic acid, but the β -form is only recoverable therefrom as an oil. Even prolonged heating with alcohol converts the β -compound into this oil. The β -compound is much more soluble in all these solvents than the α -form. Both are insoluble in alkalis and dilute mineral acids; strong sulphuric acid dissolves both with a deep red coloration, which turns green on the addition of a crystal of potassium dichromate; both are converted into tarry products by strong hydrochloric or nitric acids, or by acetic chloride; both reduce Fehling's solution when warmed with it. When pure, the α -hydrazone melts at 106°, the β - at 158—159°. Determinations of the molecular weight by Raoult's method showed that each has a simple molecule. Benzaldehyde yields the same compound, $C_{17}H_{15}N_4$, with each; it crystallises in small, white plates and melts at 215—216°, but has not been further investigated. Phenylhydrazine in acetic acid solution yields with each the same benziledi-phenylhydrazone melting at 225°. The β -hydrazone is converted into the α -form by boiling it for some time in alcoholic solution with phenylhydrazine (2 mols.).

L. T. T.

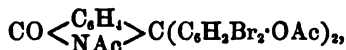
Condensation of Phthalides with Phenol. By G. ERRERA and G. GASPARINI (*Gazzetta*, 24, i, 70—81).—*Imidophenolphthaleïn*, $CO < \begin{smallmatrix} C_6H_4 \\ NH \end{smallmatrix} > C(C_6H_4OH)_2$, is formed on heating a mixture of phthalimide, phenol, and stannic chloride at 115—120° for five hours; it is ultimately obtained in hard, colourless, lustrous, acicular crystals containing 1 mol. of benzene of crystallisation, which is lost on exposure to the air. It melts at 252°, undergoing slight decomposition, and does not combine with hydroxylamine; the latter fact is in favour of Bernthsen and Friedländer's view, that free phenolphthaleïn has a quinonoid structure, whilst its metallic derivatives are salts of a true carboxylic acid. *Imidophenolphthaleïn* is insoluble in benzene or dilute mineral acids, but readily soluble in alkalis, alkali carbonates,

alcohol, or acetic acid. It does not yield Burkhardt's diimidophenolphthaleïn (Abstr., 1878, 836) when heated with aqueous ammonia in a sealed tube at 160—170°; this is perhaps accounted for by the fact that the authors were unable to prepare Burkhardt's diimidophenolphthaleïn.

Diacetylimidophenolphthaleïn, $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NH} \end{smallmatrix} > (\text{C}_6\text{H}_4 \cdot \text{OAc})_2$, prepared by heating the imidophthaleïn with acetic anhydride, is obtained as a colourless, crystalline powder melting at 254—256°.

Tetrabromimidophenolphthaleïn is prepared by heating tetrabromophenolphthaleïn with ammonia or by brominating imidophenolphthaleïn; the former method was employed by Burkhardt (*loc. cit.*). It is obtained in minute, orthorhombic crystals melting and decomposing at about 310°. On treating its alcoholic solution with nitrous acid, a yellow crystalline substance was obtained which gave unsatisfactory numbers on analysis; the mother liquors seem to contain a dinitrobromophenol [$\text{OH} : \text{Br} : (\text{NO}_2)_2 = 1 : 2 : 4 : 6 ?$].

Triacetyltetrabromimidophenolphthaleïn,



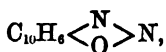
is prepared by boiling the above tetrabromo-derivative with acetic anhydride; it crystallises in colourless, birefringent octahedra melting at 176—178°, and dissolves in concentrated sulphuric acid yielding a characteristic violet solution. W. J. P.

Naphthyl Iodochlorides and Moniodosonaphthalenes. By C. WILLGERODT (*Ber.*, 27, 590—593).—The *naphthyl iodochlorides*, $\text{C}_{10}\text{H}_7\text{ICl}_2$, were prepared by passing chlorine into cooled chloroform or acetic acid solutions of the idonaphthalenes. The α -compound is an orange, apparently amorphous, very unstable substance, and decomposes at 30—45° when heated. The β -isomeride forms yellow needles, and decomposes at 56—61°. When these compounds are shaken with excess of dilute aqueous soda, they are converted into the corresponding *idosonaphthalenes*, $\text{C}_{10}\text{H}_7\text{IO}$. Of these the α -compound, which was not obtained quite pure, was amorphous, yellowish-grey in colour, perfectly stable at the ordinary temperature, and decomposed when heated to 85—125°. The β -isomeride is an amorphous, yellowish-grey substance, and decomposes noiselessly at 127—128°. C. F. B.

Isomerism of Diazo-compounds. By E. BAMBERGER (*Ber.*, 27, 679—684).— β -Diazonaphthalene, on oxidation with potassium ferricyanide in alkaline solution, yields the following three compounds:—*Naphthalene-2 : 1-diazoide*, $\text{C}_{10}\text{H}_7 < \begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix} > \text{N}$, crystallising in golden yellow needles, or large quadratic plates, and melting at 76°; β -*naphthalenediazoic acid*, $\text{C}_{10}\text{H}_7 \cdot \text{NH} \cdot \text{NO}_2$, crystallising in colourless, highly lustrous needles, which melt at 131.5—136°, according to the rapidity of heating; β -*isodiazonaphthalene* (β -*naphthyl nitrosamine*), $\text{C}_{10}\text{H}_7 \cdot \text{NH} \cdot \text{NO}$, which is deposited in crystalline flocks, consisting of

slender, colourless needles. The relative quantity in which these substances are formed depends on the experimental conditions; β -isodiazonaphthalene is obtained by the action of concentrated soda on β -diazonaphthalene; it is a tolerably strong acid, and is distinguished from the isomeric β -diazonaphthalene by its sparing solubility, its inability to combine with phenols in alkaline solution to form azo-dyes, and the stability of its alkaline solution. In presence of acids, the compound is rapidly converted into diazonaphthalene, it is very unstable at ordinary temperatures, and has therefore not been analysed. By the action of potassium ferrieyanide, β -iso diazonaphthalene is readily converted into β -naphthalenediazoic acid (see above). With methylic iodide, β -naphthylmethylnitrosamine, $C_{10}H_7 \cdot NMe \cdot NO$, is formed, and crystallises in colourless, lustrous, feathery needles, melting at 86° , it is readily volatile with steam, and gives the Liebermann reaction. The sodium salt crystallises from dilute soda in silvery, lustrous plates: it decomposes on heating; in aqueous solution it is somewhat unstable, and on boiling, nitrogen is evolved, and the solution becomes red. The barium, lead, zinc, and silver salts are colourless, crystalline, and sparingly soluble, the last explodes on heating.

The following compounds are formed by the action of potassium ferrieyanide on α -diazonaphthalene in alkaline solution:—*azomaphthalene*, $C_{10}H_7 \cdot N \cdot N \cdot C_{10}H_7$; α -naphthylamine; *naphthalenediazoic acid*, $C_{10}H_7 \cdot NH \cdot NO_2$, crystallising in golden, yellow-bronze, lustrous plates or needles, and melting at 118° ; *naphthalene-1 : 2-diazoide*,



crystallising in thick, amber-coloured, lustrous plates, melts at 95° . The last compound, on reduction, is converted into ammonia, and α -amido- β -naphthol, from which it is regenerated by means of the diazo-reaction.

α -Isodiazonaphthalene (α -naphthylnitrosamine) is prepared like the β -derivative, which it closely resembles, by the action of soda on α -diazonaphthalene; it is stable in alkaline solution, but in presence of acids is quickly converted into diazonaphthalene.

Paradiazosulphanilic acid, like the diazonaphthalenes, also yields an isomeric compound by the action of soda; in presence of acids, the reverse change takes place; the reaction is being further investigated. The interaction of silver diazobenzene and methylic iodide at 0° has also been partially studied, a considerable number of products are formed, the chief being iodobenzene.

J. B. T.

Nitro- β -naphthaquinone. By T. ZINCKE and O. NEUMANN (*Annalen*, 278, 173—207).—When finely-powdered nitro- β -naphthaquinone is dissolved by warming in methylic alcohol, and the solution allowed to remain in the cold, a compound, $C_{12}H_{10}NO_6$, is obtained, which, when pure forms colourless crystals, and melts at 143° , with darkening and evolution of gas; it dissolves readily in hot absolute alcohol and other solvents, but the crystals which separate on cooling are yellowish. The constitutional formula

$\text{C}_6\text{H}_4\cdot\text{CO}-\text{C}(\text{OH})\cdot\text{OMe}$
 $\text{CH}(\text{OMe})\cdot\text{C}\cdot\text{NO}\cdot\text{OH}$, (α -methoxy- β -nitrodiketohydronaphthalene methoxide), explains its reactions. Cold sulphuric and nitric acid or hot acetic acid decompose the compound, regenerating nitro- β -naphthaquinone, whilst the products of the actions of alkalis appear to be the same as those from β -nitronaphthaquinone.

When the last-described compound is dissolved in a solution of bleaching powder, a mixture of *orthodichloronitromethoxyethylbenzoyl-carboxylic acid*, $\text{NO}_2\cdot\text{CCl}_2\cdot\text{CH}(\text{OMe})\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COOH}$, and its *methyl salt* is obtained. The acid crystallises from a mixture of light petroleum and benzene in transparent tables, and melts at 116° ; the *methyl salt* melts at 90° . When the acid is heated with acetic chloride in a sealed tube at 120 – 130° , it yields the lactone $\text{CO}\cdot\text{O}$
 $\text{C}_6\text{H}_4 > \text{CH}\cdot\text{CCl}_2\cdot\text{NO}_2$, which, if heated with potassium acetate, gives dichloromethylenephthalide (compare Zincke and Latten, Abstr., 1892, 1231).

If the acid just described is treated with chromic acid or bleaching powder solution, *orthodichloronitromethoxyethylbenzoic acid*, $\text{NO}_2\cdot\text{CCl}_2\cdot\text{CH}(\text{OMe})\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is obtained; this melts at 187° , and its *methyl salt* at 89° (compare also *loc. cit.*). The lactone mentioned above is formed when the acid is heated with sulphuric acid or acetic chloride.

Orthodichloronitromethoxyethylbenzoic acid and the lactone obtained from it (see above) both yield homophthalic acid when heated with hydriodic acid and phosphorus in a sealed tube at 160 – 180° .

The compound, $\text{C}_6\text{H}_4\cdot\text{CO}-\text{C}(\text{OMe})\cdot\text{OH}$,
 $\text{CH}(\text{OMe})\cdot\text{CCl}\cdot\text{NO}_2$, is formed by passing chlorine into a solution of α -methoxy- β -nitro-diketohydronaphthalene methoxide in chloroform; it crystallises in lustrous needles, melts between 117° and 123° , and, when heated with acetic chloride, yields the *dihydroxy*-derivative, $\text{C}_6\text{H}_4\cdot\text{CO}-\text{C}(\text{OH})_2$,
 $\text{CH}(\text{OMe})\cdot\text{CCl}\cdot\text{NO}_2$, which melts at 137° ;

the chlorinated methoxide is regenerated from the latter by treatment with methyl alcohol. *Orthochloronitromethoxyethylbenzoyl-carboxylic acid*, $\text{OH}\cdot\text{NO}\cdot\text{CCl}\cdot\text{CH}(\text{OMe})\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COOH}$, is obtained by treating the chlorinated methoxide with alkali; it forms small, colourless crystals, and melts at 189° . The *methyl salt* melts at 100° ; the *acetyl* derivative, $\text{C}_{11}\text{H}_5\text{ClAcNO}_6$, obtained by the action of acetic chloride on the acid at 120 – 130° , is an indifferent compound melting at 179° ; the *acetyl* derivative of the methyl salt melts at 115° . When orthochloronitromethoxyethylbenzoyl-carboxylic acid is treated with bleaching powder solution, dichloromethoxyethylbenzoic acid (see above) is formed; whilst by the action of chromic acid orthochloromethoxyethylbenzoic acid (Zincke and Latten *loc. cit.*) is obtained.

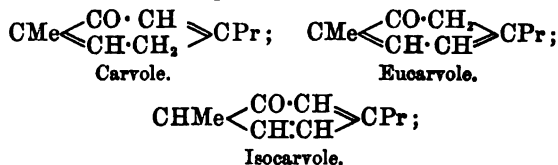
A. R. L.

Orientation in the Terpene Series. By A. v. BAETTER (*Ber.*, 27, 810–816; compare this vol., i, 92 and 252).—Hydrobromocarvole, $\text{C}_{10}\text{H}_{16}\text{O}\cdot\text{HBr}$, has been previously obtained by Goldschmidt and VOL. LXVI. i.

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Kisser (Abstr., 1887, 923), by the action of hydrogen bromide on carvole, and is prepared by the action of hydrogen bromide in glacial acetic acid solution on carvole, at low temperatures; it is deposited from ether in camphor-like, crystalline masses, has no smell, and melts at 32°. Part of the substance melts at a lower temperature; it is identical with hydrobromocarvole in its chemical properties, and the reason for the difference in melting point has not yet been determined. Hydrobromocarvoxime is formed by the action of hydroxylamine on the preceding compound, and melts at 136°, instead of 116° as stated by Goldschmidt and Kisser, who obtained it by treating carvoxime with hydrogen bromide in methylic alcoholic solution (*loc. cit.*).

The action of methylic alcoholic potash (1 : 2) at low temperatures on hydrobromocarvole converts it into *eucarvole*, $C_{10}H_{14}O$, not into carvole, as Goldschmidt and Kisser found; this boils at 210—215°, and is partially decomposed into carvacrole; under 25 mm. pressure it boils at 104—105°, without decomposition; the sp. gr. = 0.948 at 20°/4°; it is optically inactive, and is quantitatively converted into carvacrole by heating for an hour at its boiling point. Eucarvole does not combine with sodium hydrogen sulphite; it derives its name from the production of a pure, deep blue colour on heating with methylic alcoholic potash; the colour is unstable, and disappears on the addition of water. The *phenylhydrazone* is oily; the *oxime* is indistinguishable from carvoxime in appearance, and melts at 106°. The following reactions show the difference between eucarvoxime, carvoxime, and isocarvoxime. (1.) By boiling with dilute sulphuric acid, carvoxime and isocarvoxime are immediately converted into carvole and carvacrole respectively; eucarvoxime is much more stable. (2.) Concentrated sulphuric acid acts on carvoxime and isocarvoxime, with development of heat and formation of crystalline compounds, which have not yet been investigated. Eucarvoxime dissolves without change. (3.) Bechmann's chromic acid mixture colours crystals of carvoxime black; crystals of isocarvoxime and eucarvoxime are not blackened. (4.) Ferric chloride in alcoholic solution gives a green coloration with eucarvoxime, and a yellow colour with carvoxime and isocarvoxime. (5.) Boiling methylic alcoholic potash is without action on carvoxime or eucarvoxime; isocarvoxime is decomposed into an oily liquid. (6.) Bromine yields apparently different crystalline compounds with all three oximes. On the assumption of the absence of the semicyclic double linkage^{4a}, the following formulæ represent the three carvoles,



isocarvole must be tautomeric with carvacrole, or converted into it with the greatest ease, as shown by the action of dilute sulphuric acid on the oxime; eucarvole is converted into carvacrole at its boiling point,

whilst carvole only yields carvacrole with difficulty. Encarvole on reduction with sodium and alcohol, yields an isomeric dihydro-carveol boiling at $217-219^{\circ}$ (corr.), and resembling menthol in odour. On oxidation with chromic acid mixture, a compound is obtained which smells of camphor, combines with hydroxylamine, but not with sodium hydrogen sulphite, and is being further investigated. Hydrobromocarvolephenylhydrazone melts at $123-124^{\circ}$, and carvolephenylhydrazone at $109-110^{\circ}$, instead of 119° and 106° respectively, as stated by Goldschmidt and Kisser.

In continuation of his past paper on terpinene, the author states that $\Delta^{(8)}$ -terpen-1-ol is formed in considerable quantity in the preparation of terpinol from terpin and oxalic acid or phosphoric anhydride; it boils at $69-70^{\circ}$, not at $69-90^{\circ}$, as stated, and is isolated by means of the blue nitrosochloride; Schimmel's liquid terpenol, under similar circumstances, does not yield any blue compound. The presence of terpinene in other terpentine oils can be detected by the production of a brown colour, or of brown flocks, on shaking with the following mixture:—Sodium dichromate (6 parts), concentrated sulphuric acid (5 parts), water (30 parts); as this is without action on the other constituents of terpentine oils, the terpinene is readily eliminated by repeated treatment with the oxidising mixture at ordinary temperatures.

J. B. T.

Quercitrin and Allied Compounds. By R. WACHS (*Chem. Centr.*, 1894, i, 50—51; from *Pharm. Post.*, 26, 529—530).—The substances investigated were quercitrin from quercitron bark; yellow colouring matters from the flower buds of *Sophora japonica*; similar substances from *Viola tricolor var. vulg.*, from the leaves of *Aesculus hippocastanum*, from those of *Thuja occidentalis*, and from the flower buds of *Capparis spinosa*. These substances are divisible into two classes, the one includes quercitrin and chestnut-quercitrin, the other contains the remainder, with the exception of thujin, which occupies an intermediate position, but its derivative thujetin differs considerably from quercetin. Quercitrin, $C_{21}H_{20}O_{11}$, contains $1H_2O$ less than chestnut-quercetin, $C_{21}H_{22}O_{12}$; the members of the second group have the formula $C_{27}H_{26}O_{16}$; on hydrolysis, the members of both groups yield compounds of the formula $C_{15}H_{14}O_7$, which are identical or isomeric with quercetin, but caper-quercetin appears to be $C_{15}H_{12}O_7$. The compounds from *Viola tricolor*, *Sophora*, *Capparis spinosa*, and *Thuja*, yield glucose on hydrolysis, in addition to isodulcitol. The amount of sugar formed on hydrolysis varies considerably, as shown in the following table.

	Sugar as isodulcite, per cent.	Quercetin, per cent.
Quercitrin	38.99	68.65
Sophorin	57.16	49.54 (sophoretin)
Viola-quercitrin	55.78	51.86
Chestnut-quercitrin ..	36.83	65.65
Caper-quercitrin	56.73	49.61
Thujin	38.16	62.25 (Thujetin)

J. B. T.

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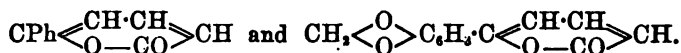
New Constituent of True Coto Bark. By G. CIAMICIAN and P. SILBER (*Ber.*, 27, 841—850).—The substance which forms the subject of this paper was obtained in the purification of cotoïn on the large scale. It forms yellowish crystals melting at 66—68°, and has the formula $C_{11}H_8O_2$. In chemical properties, it is closely allied to paracotoïn, which the authors consider to be dioxymethylene-phenylcoumalin, but differs from it by the absence of the dioxymethylene group, so that it receives the name (provisionally) of *phenylcoumalin*. It may be purified by treatment with hydrobromic acid, which forms an unstable compound with it, and this decomposes gradually, leaving the original substance, which then only requires to be freed from acid by dissolving it in alcohol and precipitating with water. It is readily soluble in ether, alcohol, acetic acid, &c., but only very sparingly in water. It dissolves in alkalis and alkali carbonates, yellow solutions being formed, which smell of acetophenone. Sulphuric acid in the cold dissolves the compound without alteration. It is, moreover, not acted on by acetic anhydride or hydriodic acid, and therefore does not contain hydroxyl- or methoxyl-groups. *Bromophenylcoumalin*, $C_{11}H_7BrO_2$, is produced by the action of bromine on a solution of the substance in chloroform, and forms yellowish crystals melting at 138—139°.

Nitric acid converts the original compound into a *mononitro-derivative*, which forms rhombic tablets melting at 161°. Like paracotoïn, the new substance reacts with phenylhydrazine, and yields a compound of the formula $C_{22}H_{22}N_4O$, which crystallises in slender, white needles, and melts at 198°. It also reacts with aniline, forming a compound which crystallises in needles, and melts at 143°.

When boiled with aqueous alkalis, phenylcoumalin yields acetophenone, and an amorphous acid which could not be obtained crystalline. When fused with potash, it gives benzoic acid, thus corresponding closely with paracotoïn. When it is heated with hydrochloric acid at 140°, phenylcoumalin is converted into a white, crystalline product which melts at 214°, and has the same composition as the original substance, of which it is probably a polymeride.

When heated with methylic iodide and alcoholic potash, phenylcoumalin is converted into a *dimethyl-derivative*, which crystallises in long, yellowish needles, melting at 100—101°. This compound corresponds with the dimethyl-derivative of paracotoïn, and is decomposed by alkalis, with formation of ethylphenyl ketone.

The properties of this new substance, and of paracotoïn itself, are, as already explained, best accounted for on the supposition that these substances are coumalin derivatives of the formulæ



They cannot, however, like the other known coumalin-derivatives, be readily converted into compounds of the pyridine series, or into the ether of the corresponding hydroxy-acid. On the other hand, dimethylcoumalin (mesitene lactone) is converted by the action of methylic iodide and potash into a trimethyl-compound, and thus resembles both the substances under discussion. The *trimethylcou-*

malin thus formed separates from water in long white needles containing $3\text{H}_2\text{O}$, and melting at $45\text{--}46^\circ$. The anhydrous substance melts at 74° .

It is not impossible that the substance described by Jobst and Hesse as dicotoïn may prove to be impure phenylcoumalin.

A. H.

Kamala and Rottlerin. By P. BARTOLOTTI (*Gazzetta*, 24, i, 1—7).—The author confirms the formula $\text{C}_{11}\text{H}_{10}\text{O}_2$, previously assigned to rottlerin, but has evidently overlooked the paper, published some months previously to his own, by A. G. Perkin (*Trans.*, 1893, 975). The author finds that rottlerin melts at $200\text{--}201^\circ$, whilst Perkin gives the melting point as $191\text{--}191.5^\circ$. The so-called “kamaline,” put into the market by Merck, of Darmstadt, is simply rottlerin.

Dibenzoylrottlerin, $\text{C}_{11}\text{H}_8\text{Bz}_2\text{O}_2$, and *rottlerin hydrazone*,



are yellow powders, which decompose on heating, and are soluble in the ordinary solvents.

The ash of kamala contains a considerable proportion of manganese.

W. J. P.

Amidopyridinecarboxylic acid. By A. PHILIPS (*Ber.*, 27, 839—840).—When ammonia is passed into a solution of quinolinic acid in benzene, the *ammonium quinolinamate*,



is formed. When heated for some time at $120\text{--}130^\circ$, this substance passes into quinolinic imide, $\text{C}_8\text{NH}_3\cdot\text{CO}\cdot\text{NH}$, which melts at 230° , and readily combines with ammonia, forming the *diamide of quinolinic acid*, $\text{C}_8\text{NH}_3(\text{CONH}_2)_2$. The free *quinolinaminic acid*,



is obtained by passing sulphurous anhydride into an aqueous solution of the ammonium salt, and forms white needles melting at 168° , with evolution of gas. When its aqueous solution is heated, it combines with water to produce ammonium hydrogen quinolinate. Quinolinaminic acid, when treated with sodium hypobromite, is readily converted into 2 : 3-*amidopyridinecarboxylic acid*, $\text{NH}_2\cdot\text{C}_8\text{NH}_3\cdot\text{COOH}$, which forms white needles, melting with evolution of gas at 210° . When heated, this compound loses carbonic anhydride, and yields α -(2)-amidopyridine identical with that described by Marckwald (*Abstr.*, 1893, i, 727). Quinolinaminic acid and the amidopyridinecarboxylic acid derived from it, have therefore the constitutions given above.

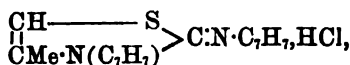
A. H.

Oxidation of Reduced Quinolines. By J. TAFEL (*Ber.*, 27, 824—826).—3-Methyltetrahydroquinoline, 1-methyltetrahydroquinoline, and tetrahydroquinoline are oxidised by treatment with mercuric acetate in the manner previously described (*Abstr.*, 1892, 1104); the yield varies from about 40 to 60 per cent. of the theoretical.

Tetrahydroquinoline-1-carboxylic acid, $\text{COOH} \cdot \text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{NH} \cdot \text{CH}_2 \end{smallmatrix}$, is prepared by the reduction of orthoquinolinecarboxylic acid with tin and hydrochloric acid, and crystallises in colourless needles melting at 163° (uncorr.), and subliming at higher temperatures. In neutral or alkaline solutions it exhibits a blue fluorescence; with dilute sulphuric acid and oxidising agents in aqueous solution, a brownish-red precipitate is produced. On oxidation with mercuric acetate, 1-quinolinecarboxylic acid is only formed in small quantity, the larger portion being decomposed into tetrahydroquinoline and carbonic anhydride. Attempts to prepare hydroxyquinoline or methoxyquinoline from the tetrahydroderivatives, have led to negative results. J. B. T.

Allylamidothiazoles and their Isomerides. By G. MARCHESINI (*Gazzetta*, 24, i, 65—70; compare this vol., i, 209).—2:5-Methyl-dibenzylamidothiazole, $\begin{smallmatrix} \text{CH} - \text{S} \\ | \quad \quad | \\ \text{CMe} - \text{N} \end{smallmatrix} > \text{C} \cdot \text{N}(\text{C}_6\text{H}_5)_2$, is prepared by heating unsymmetrical dibenzylthiocarbamide with chloracetone in alcoholic solution in a reflux apparatus; it crystallises in long, yellowish needles melting at 50° , and is soluble in alcohol or ether. It is precipitated unaltered from its alcoholic solution, and gives no precipitate with alcoholic silver nitrate.

1:2:5-Benzylmethylbenzylimidothiazoline hydrochloride,



is prepared by heating symmetrical dibenzylthiocarbamide and chloracetone in alcoholic solution; it crystallises in small, white scales, and melts at 194° . The hydrobromide is obtained in small, white laminae, melting at 198° , and is very soluble in alcohol.

The product obtained by heating benzylic iodide with 2-phenylamidothiazole at 150° , in an oil bath, contains a substance having the composition of 1:2:5-benzylphenylbenzylimidothiazoline; it forms white crystals melting at 138° , and is soluble in alcohol or ether. A small proportion of a substance melting at 128° accompanies it.

W. J. P.

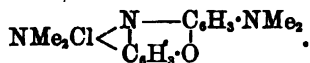
Pyrazole Compounds. By L. BALBIANO and G. MARCHETTI (*Gazzetta*, 24, i, 8—14; compare Abstr., 1893, i, 672).—Dibenzoyl-3:5-dimethylpyrazole is obtained by heating 3:5-dimethylpyrazole with benzoic chloride at 250 — 260° ; it crystallises in small, white prisms melting at 124 — 124.5° , and is soluble in ether or hot alcohol. On warming with sodium ethoxide in alcoholic solution, it yields 4-benzoyl-3:5-dimethylpyrazole, $\text{NH} < \begin{smallmatrix} \text{CMe} \cdot \text{CBz} \\ \text{N} = \text{CMe} \end{smallmatrix}$; this crystallises in lustrous, white needles, which contain $2\text{H}_2\text{O}$, and melts at 59 — 60° . It is soluble in alcohol or ether, and is not attacked by alcoholic potash. On treating its solution in aqueous alcoholic potash with ammoniacal silver nitrate solution, the argento-derivative, $\text{C}_8\text{N}_2\text{Me}_2\text{BrAg}$, separates as a caseous mass.

4-Benzoyl-1 : 3 : 5-triphenylpyrazole is prepared by heating 1 : 3 : 5-triphenylpyrazole with benzoic chloride at 250—260°; it crystallises in yellowish, lustrous needles melting at 172—173°, and is sparingly soluble in alcohol or ether. It is not attacked by alcoholic potash. No benzoyl-derivative of 1 : 4 : 5-phenylmethylpyrazole could be obtained. Attempts to prepare a trimethylenediamine isomeric with cadaverine by reducing 3 : 5-dimethylpyrazole with tin and hydrochloric acid also failed.

W. J. P.

Oxazines and Eurhodines. By C. LAUTH (*Compt. rend.*, 118, 473—476).—Nitrosodimethylaniline was reduced with zinc and hydrochloric acid, and then treated with sodium thiosulphate, hydrogen carbonate, and carbonate. The mercaptan thus obtained was mixed with an acid solution of diethylamidophenol, and the mixture oxidised with potassium dichromate, and neutralised with sodium carbonate. The dark blue solution was boiled, and the precipitate collected, washed, dissolved in dilute hydrochloric acid, precipitated with sodium chloride, redissolved in sodium carbonate solution, and precipitated with zinc and sodium chlorides, and finally crystallised from alcohol.

The blue-violet colouring matter thus obtained is somewhat soluble in water and alcohol, very slightly soluble in sodium carbonate solution, more soluble in ammonia. Ether removes only traces from the ammoniacal solution. It dissolves in concentrated sulphuric acid, forming a red-violet solution, and in concentrated hydrochloric acid, forming an olive-green solution. Dilute acids form pure blue solutions. The colouring matter dyes silk, wool, and cotton mordanted with tannin, a violet-blue. It contains no sulphur, and must be regarded as an oxazine of the constitution



Direct oxidation of a mixture of amidodimethylaniline and diethylamidophenol yields a blue compound which, however, is very different from the oxazine, and has the properties of an indamine. It is very soluble in alkalis, is completely decomposed by acids and by boiling with water, and when boiled with aniline acetate in presence of a dichromate it yields a safranine. It may be regarded as having the constitution $\text{NMe}_2\text{Cl} < \begin{array}{c} \text{N} \cdot \text{C}_6\text{H}_5 \cdot (\text{OH}) \cdot \text{NMe}_2 \\ | \\ \text{C}_6\text{H}_4 \end{array}$. The author did not

succeed in converting this indamine into the oxazine, but its formation indicates that when the mixture of mercaptan and diethylamidophenol is oxidised, there is first formed a sulphonated thioindamine, and when this is boiled with water in presence of an oxidising agent, the S·SO₃H group is eliminated, and the oxygen of the hydroxyl is fixed on the two nuclei in a manner analogous to the formation of methylene-blue.

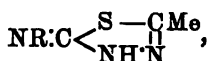
The compound described is different from that obtained by the action of nitrosodimethylaniline on diethylamidophenol, but, in view of the irregular behaviour of nitrosodimethylaniline, the latter reac-

tion cannot be regarded as evidence against the formation of an oxazine. Moreover, when equal molecular proportions of metamidodimethylaniline and the sulphonated mercaptan of paramidodimethylaniline are oxidised, tetramethyleurhodine is formed by a reaction analogous to that which gives rise to an oxazine. C. H. B.

Derivatives of Thiosemicarbazides. By G. PULVERMACHER (*Ber.*, 27, 613—630; compare this vol., i, 76).—Phenyl-, methyl-, and allyl-thiocarbimides, with hydrazine hydrate, in cooled alcoholic solution, yield thiosemicarbazides, $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}_2$, and these, with aldehydes $\text{R}\cdot\text{CHO}$, form compounds $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{N}\cdot\text{CHR}$. With crystallisable formic acid, they yield formyl derivatives,



which, when boiled with acetic chloride, lose water, and yield bases, $\text{NR}\cdot\text{C} < \begin{smallmatrix} \text{S} - \text{CH} \\ | \\ \text{NH} \cdot \text{N} \end{smallmatrix}$; phenylthiosemicarbazide, however, yields the base directly, without the intermediate formation of a formyl derivative. To these bases, the name of *alkylimidothiobiazolines* is given, in accordance with Freund's nomenclature (*Abstr.*, 1890, 1440). They yield nitroso-derivatives, and, with acetic anhydride, acetyl-derivatives. When heated at 100° with methylic iodide, *n*-methyl-derivatives, $\text{NR}\cdot\text{C} < \begin{smallmatrix} \text{S} - \text{CH} \\ | \\ \text{NMe} \cdot \text{N} \end{smallmatrix}$, are formed which yield methylamine when decomposed by hydrochloric acid at 180° . Isomeric *c*-methyl-derivatives,



are obtained by the action of acetic chloride on the thiosemicarbazides; these also yield nitroso-, acetyl-, and *n*-methyl-derivatives, the last being $\text{NR}\cdot\text{C} < \begin{smallmatrix} \text{S} - \text{CMe} \\ | \\ \text{NMe} \cdot \text{N} \end{smallmatrix}$. These bases are very stable; they are not affected when boiled with 15 per cent. hydrochloric acid or with caustic soda, or when reduced with tin and hydrochloric acid, nor does boiling with freshly precipitated mercuric oxide remove any sulphur from them.

Phenylthiosemicarbazide, which forms colourless, hexagonal prisms, and melts with decomposition at 140° , is decomposed by boiling with various reagents; with hydrochloric acid, it yields phenylthiocarbamide; with soda, phenylcarbamide; with mercuric oxide, phenylcarbamine and mercuric sulphide; with acetic acid, hydrogen sulphide and the base, $\text{C}_{14}\text{H}_{14}\text{N}_4\text{S}_2$, obtained by Freund and Wischewiansky (this vol., i, 96). Its *benzal*-, *salicylal*-, *cinnamylidene*-, and yellow *metanitrobenzal*-derivatives melt respectively at 191° , 183° , 175 — 176° , and 193 — 194° . *Phenylimidothiobiazoline* melts at 173° ; the *hydrochloride* contains 1HCl . The *nitroso*- and *acetyl*-derivatives melt at 80 — 81° and 142° respectively; the yellow *n*-methyl-derivative melts at 258° , its yellow *hydriodide* at 203 — 204° ; the *c*-methyl-derivative at 193 — 194° , its *hydrochloride* ($\frac{1}{2}\text{HCl}$) at 190 — 191° , and its yellow *nitroso*- and colourless *acetyl*-derivatives at 114 — 115° and 148° respectively; the greenish *c*:*n*-dimethyl derivative melts at 193 — 194° , its

hydriodide at 198°. The action of benzoic chloride on phenylthiosemicarbazide is anomalous; two products are obtained melting at 281° and 200° respectively, neither of which are basic, one having even slightly acid properties.

Methylthiosemicarbazide melts at 137—138°, its *benzal derivative* at 160°, and its *formyl derivative* at 167—168°; the latter is decomposed into its components by boiling with aqueous soda. *Methylimidiothiobiazoline* melts at 65—66°, the *hydrochloride* at 245°. The *hydriodide* of the *n-methyl derivative* melts at 232—233°; the *c-methyl derivative* at 112°, its *hydrochloride* at 211—212°, and *nitroso derivative* at 56°; the *c:n-dimethyl derivative* at 248—249°, its *hydriodide* at 150—151°.

Allylthiosemicarbazide melts at 98—99°; its *benzal-, salicylal-, cinnamylidene-, and metanitrobenzal-derivatives* respectively at 124—125°, 149—150°, 165—166°, and 163°; its *formyl-derivative* at 128—129°. *Allylimidothiobiazoline* melts at 73°; the *hydrochloride* at 128—130°, the *acetyl-derivative* at 57°. The *hydrochloride* of the *n-methyl derivative* melts at 176—177°; the *c-methyl derivative* forms small plates, its *hydrochloride* melts at 172—173°, and its *acetyl derivative* at 77—78°; the *hydriodide* of the *c:n-dimethyl derivative* melts at 115—116°. With benzoic chloride, allylthiosemicarbazide yields a *benzoyl-derivative*, melting at 171°, and this, when heated with acetic chloride, is converted into *allylimido-c-phenylthio-biazoline*, which melts at 115°, its *hydrochloride* at 113°, and its *acetyl- and nitroso-derivatives* at 123—124° and 95° respectively. C. F. B.

Constitution of the Carbazines. By C. D. HARRIES and E. LOEWENSTEIN (*Ber.*, 27, 861—868).—Diphenyldimethylthiocarbazine, $\text{CS}(\text{NH}\cdot\text{NMePh})_2$, melts sharply at 176°, and not indefinitely at 168°, as stated by Stahel (*Annalen*, 258, 242). *Diphenyldimethylthiosemicarbazide*, $\text{NMePh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NMePh}$, is obtained by heating a mixture of methylphenylhydrazine, methylaniline, and carbon bisulphide with alcohol on the water bath. It forms large, rhombic prisms melting at 113°, and is insoluble in light petroleum and in water. It is dissolved without alteration by hydrochloric acid, and is not decomposed by yellow mercuric oxide.

Phenylmethylthiosemicarbazide, $\text{NMePh}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, is obtained from phenylmethylhydrazine sulphate and ammonium thiocyanate in alcoholic solution. It crystallises in microscopic octohedra, melts at 187°, and is slightly soluble in ether, almost insoluble in light petroleum and in benzene.

Phenylmethylthiocarbazine, $\text{C}_6\text{H}_5\cdot\text{N}(\text{Me})\cdot\text{S}\cdot\text{CH}_2$, is prepared by boiling diphenyldimethylthiosemicarbazide with hydrochloric acid in dilute alcoholic solution, methylaniline being also formed. The *hydrochloride*, $\text{C}_6\text{H}_5\cdot\text{N}(\text{Me})\cdot\text{S}\cdot\text{HCl}$, crystallises in fine needles, and the *platinochloride* in yellow, microscopic needles, as does also the *aurochloride*. The *picrate* crystallises in groups of yellow needles, and melts and decomposes at 240°. The free base melts at 123°, and is in every respect identical with the compound obtained by Fischer and Besthorn (*Annalen*, 212, 316) by the action of methylic iodide on phenylthiocarbazine.

When it is boiled in alcoholic solution with methylic iodide, *phenylmethylthiocarbazonium iodide*, $C_6H_5N_2SMeI$, is formed, and this crystallises in groups of light yellow needles melting with decomposition at 280° . *Bromophenylmethylthiocarbazine*, $C_6H_4BrN_2S$, is obtained by direct bromination, and melts at 106° , whilst the *hydrobromide* melts with decomposition at 250° .

On heating the base with nitric acid, a *dinitro-compound* is produced, which forms very sparingly soluble, orange-yellow needles melting at 250° with decomposition.

When phenylmethylthiocarbazine is fused with potash, it forms *orthomethylamidophenyl mercaptan*, soluble in acids and alkalis. This compound if kept, is converted into the corresponding *bisulphide*, $S_2(C_6H_4.NHMe)_2$, which forms odourless, four-sided, golden-yellow tablets melting at $67-68^\circ$, and is reconverted by zinc-dust and dilute sulphuric acid into the mercaptan. Phenylthiocarbazine undergoes a similar decomposition when fused with potash, *orthamidophenyl mercaptan* being produced, but the decomposition does not take place so readily as with the methyl-derivative. This reaction renders it probable that in the formation of carbazine-derivatives from the thiosemicarbazides, the sulphur atom enters the benzene ring and forms part of a new six-atom ring. The formula thus obtained,

$C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{S} - \text{CH} \end{smallmatrix}$, also agrees with the formation of phenylmethylthiocarbazine from diphenylmethylthiosemicarbazide, in which the phenyl- and methyl-groups are combined with the same nitrogen atom, whereas the formula proposed by Fischer and Besthorn, $NPh \begin{smallmatrix} \text{NH} \\ \text{CS} \end{smallmatrix}$

is inconsistent with both of these facts.

Diphenylmethylthiosemicarbazide, $NEtPh \cdot CS \cdot NH \cdot NMePh$, is prepared in a similar manner to the dimethyl derivative. It is very soluble in the usual solvents, crystallises in colourless plates, and melts at $83-84^\circ$. The corresponding *carbazine* melts at 176° .

Phenylmethylhydrazine also reacts with aniline in a similar manner. The substance formed appears to be identical with the compound melting at 154° described by Fischer. A. H.

Isopipicoline and the Asymmetric Nitrogen Atom. By A. LADENBURG (*Ber.*, 27, 853-858).—Coniine exists in four modifications (*Abstr.*, 1893, i, 442), and the author has proposed to account for the fourth of these, isoconiine, by a theory involving the existence of an asymmetric nitrogen atom. Attempts to obtain evidence on this point by splitting up nitrogen derivatives into optically active isomerides have been made, but without success. Tetrahydroquinoline and tetrahydroisoquinoline were converted into the tartrates, but no different modifications could be obtained by the fractional crystallisation of these. *Tetrahydroisoquinoline hydrogen tartrate* melts at $140-142^\circ$ and forms hemihedral rhombic crystals. The axial ratio of these is $0.95008 : 1 : 1.80913$, and the principal angles $(110) : (1\bar{1}0) = 87^\circ 4'$; $(001) : (101) = 60^\circ 56'$.

d-α-Pipicoline hydrochloride, when it is distilled over zinc-dust, also yields a base possessing a lower rotatory power, and to this has

been given the name of isopiecoline. That this is a definite isomeride of α -piecoline and not simply a mixture of the dextro- with a little of the lævo-variety, formed during the distillation, is proved by the fact that the hydrogen tartrate of this base solidifies completely on crystallisation, whereas that of r -piecoline always leaves a certain amount of uncrystallisable syrup behind. An examination of the base prepared from the last fraction of isopiecoline hydrogen tartrate, moreover, proved that it had a much greater rotatory power than would have been the case if the original base had consisted of a mixture of the d -base with the r -base. The existence of isopiecoline may, therefore, be considered to be definitely established.

Another method proposed by the author to distinguish between an optical isomeride of less rotatory power and a mixture of an optically active base with a portion of the inactive modification of the same base, consists in converting the pure active form into some other active derivative, and thus obtaining the ratio of the rotations of these two. The substance to be tested is then similarly treated. If it be a mixture of the optically active with the inactive form, the same ratio should be obtained in the second case as in the first, provided the proportions of the active and inactive forms are not changed by the reaction. An experiment of this kind, carried out with isopiecoline, gave an indecisive result, the difference between the two ratios being almost within the limit of error, which was found to be about 8 per cent.

d -Methyl- α -piecoline, which was employed in this experiment, boils at 128–131°, and has a specific gravity of 0.825 at 16° and a rotatory power, $[\alpha]_D = +64.99^\circ$. A. H.

Pure d-Coniine. By A. LADENBURG (*Ber.*, 27, 858–859).—Pure coniine boils at 166–167° and has a specific rotation equal to $[\alpha]_D = +15.6^\circ$. This number is identical with that given by Schiff (*Annalen*, 166, 94), which has been mistaken by Landolt for the angle of rotation and used by him for the calculation of the specific rotation. The platinochloride of this substance is completely soluble in a mixture of alcohol and ether. When its alcoholic or aqueous solution is evaporated, it solidifies at once on cooling, whereas the platinochloride of the impure material generally remains oily for some time.

A. H.

Crystalline Form of Isoconiine Platinochloride. By A. LADENBURG (*Ber.*, 27, 859–861).—This salt is dimorphous.

The form melting at 175° crystallises in the rhombic system, the axial ratio being 0.6971 : 1 : 0.38145 and the principal angles (120) : (010) = 35° 39'; (101) : ($\bar{1}$ 01) = 57° 22.5'. The crystals are of two types, both being columnar, one type parallel to the vertical axis, the other parallel to the macrodiagonal.

The second form, melting at 160°, crystallises in monosymmetric tablets, the constants of which are:—Axial ratio, 1.3919 : 1 : 1.0570. Axial angle, 64° 30'. Principal angles:—(110) : (100) = 51° 29'; (110) : (001) = 74° 27'; (11 $\bar{1}$) : (00 $\bar{1}$) = 60° 11'. A.H.

Isoconiine and Asymmetric Nitrogen. By L. SIMON (*Bull. Soc. Chim.*, [3], 9, 949–952).—A rejoinder to Ladenburg (this vol.,

i, 213). It is true that stereoisomerism is not possible in piperidine itself, but it can certainly occur in disubstituted piperidines of the type represented by the formula $\text{CH}_2 \langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CR}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \rangle \text{NH}$. The cyclic arrangement of such a ring changes as it is viewed from one side or the other, and if the third bond of the nitrogen atom is not in the plane of the ring, there will be two different stereometric configurations accordingly as it lies on the one side or the other of the plane. If, however, the bond is in the plane of the ring, there will be no such isomerism. Ladenburg's failure to isolate isomerides of the hydroquinolines seems to show that the latter is the case.

The same reasoning applies to monosubstituted piperidines such as the coniines. If the third nitrogen bond is not in the plane of the ring, dextro- and lævo-coniine will each yield two isomerides, in the formula of one of which the bond is on the same side of the ring as the propyl-group, in that of the other, on the opposite side—Ladenburg's isoconiine is one of these isomerides.

Asymmetric nitrogen may serve, therefore, to modify the rotatory power due to asymmetric carbon, but cannot alone cause the rotation.
JN. W.

Aconitine. By W. R. DUNSTAN (*Ber.*, 27, 664).—A reply to Freund and Beck (see note, this vol., i, 263).

Aconitine. By M. FREUND and P. BECK (*Ber.*, 27, 720—733; compare this vol., i, 263).—This paper consists in the main of an amplification of that above referred to, the details of the experimental work being given in full.

Apoaconitine appears not to exist, and the so-called japaconitine, $\text{C}_{28}\text{H}_{48}\text{O}_2\text{N}_2$, is also identical with ordinary aconitine. The molecular weight of the latter in benzene solution was found to be 663 (calc. 645). The melting point of aconitine varies according to the rate at which it is heated. It is usually stated to be 188—189°, but when the temperature is rapidly raised, it is observed to be 197—198°. The α - and β -aurochlorides, the nitrate, and the hydrobromide all give numbers on analysis which agree well with the formula proposed by the authors (*loc. cit.*).

Picraconitine (isaconitine) aurochloride is amorphous, and melts indefinitely at 125—135°. The colourless compound melting at 204°, obtained by Dunstan and Harrison by the gradual evaporation of its alcoholic solution, could not be obtained. The hydriodide forms splendid white crystals which soften at 201—202°, and then melt at 204—205°. The hydriodide of isaconitine melts, according to Dunstan, at 246°. *Picraconitine nitrate* is only slightly soluble in water, and crystallises from alcohol in coarse prisms, which become yellow at 210°, and decompose at 240—250°.

The second crop of crystals from the liquid obtained by boiling aconitine with water consists of the acetate of picraconitine. The mother liquor, after the removal of all the picraconitine, yielded, after neutralisation and evaporation, a residue of aconine, which was converted into the hydrochloride. This substance agrees in proper-

ties with the compound described by Dunstan and Passmore, but appears from a number of analyses to have the formula



and not $\text{C}_{26}\text{H}_{41}\text{NO}_{11}, \text{HCl}, 2\text{H}_2\text{O}$, which has been ascribed to it.

Aconine is also formed by the action of boiling alcoholic potash on picroconitine.

When picroconitine is boiled with acetic anhydride, it yields, along with an amorphous substance, an *acetyl-derivative*, $\text{C}_{26}\text{H}_{44}\text{AcNO}_{10}$, which crystallises from alcohol in prisms melting at $255-256^\circ$.

Aconine and picroconitine contain the four methylic groups originally present in the molecule of aconitine.

A. H.

Ptomaine from Damaged Cheese. By C. LEPIERRE (*Compt. rend.*, 118, 476—478).—1 kilo. of a ripe cheese from ewes' milk, which gave rise to digestive troubles when eaten, was found to be free from metallic poisons, and yielded no poisonous proteid or albumose, but when treated by Gautier's process, it gave some decigrams of a well crystallised base of the composition $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_4$. It has no odour, but a bitter taste, is slightly acid to phenolphthalein, dissolves very slightly in water, but is soluble in alcohol, and yields a *hydrochloride*, which is very soluble and crystallises in large needles. The *platinochloride* and the *aurochloride* are also crystallisable. The specific rotatory power of the base is $[\alpha]_D = +11.3^\circ$ in aqueous solution. Its salts are precipitated by acid sodium phosphomolybdate, picric acid, and solution of iodine in potassium iodide, but not by tannin.

When administered by ingestion to a guinea pig, the base produced diarrhoea; but an aqueous solution of the hydrochloride, when injected into the vein of a rabbit's ear, produced no ill effects.

No other definite bases were isolated, but the bases not precipitated by cupric acetate yielded small quantities of pyrroline when distilled with barium hydroxide.

Other cheeses of the same kind and age yielded no similar base.

C. H. B.

Crystallisation of Egg-albumin. By S. BONDZYŃSKI and L. ZOJA (*Zeit. physiol. Chem.*, 19, 1—18).—Elementary analysis of egg-albumin has, in the hands of different observers, yielded different results. This appears to be in part owing to the fact that sometimes the globulin in egg-white has not been previously separated from the albumin. But in those cases where the albumin itself has been analysed, discordant results have suggested that egg-albumin is not a single substance but a mixture of albumins. In the present research, facts were discovered which bear out this supposition; the method adopted was that of Hofmeister.

Large quantities of egg-white were half saturated with ammonium sulphate, and after the globulin thus precipitated had been removed by filtration the albumin slowly crystallised out from the filtrate. The fractional method of crystallisation was adopted, and the different fractions examined; they were found to differ in their properties

(solubilities, temperature of heat coagulation, and specific rotation) and slightly in elementary composition.

Attempts to crystallise egg-globulin, and the proteïds of serum, led to negative results.

W. D. H.

Caseïns and Fibrins. By M. ARTHUS (*J. Pharm.*, 29, 101—105).—The name casein is given to the principal proteïd of milk, and caseum to the curd produced by rennet. Caseogen is a term given to the casein when that substance is modified by rennet added to decalcified milk. It coagulates on heating, and appears to correspond to the meta-casein of Sir W. Roberts (see Edkins, *Abstr.*, 1891, 1272). The lacto-albumin of milk does not belong to this group.

Fibrin and fibrinogen form a group analogous to the caseïns.

W. D. H.

Nucleoproteïds. By O. HAMMARSTEN (*Zeit. physiol. Chem.*, 19, 19—37).—In diabetes, there is no longer any doubt that in many cases the sugar originates from proteïds. A knowledge of glucoproteïds (proteïds from which sugar is obtainable by hydrolytic agents) is therefore of practical importance. Such proteïds are obtainable from the mammary gland, the liver, and the pancreas; the present paper relates, however, only to that obtained from the pancreas. The finely divided organ is rapidly boiled in water, and filtered; the filtrate is clear, and yellow in colour. After cooling, if 1—2 per cent. of hydrochloric or 5—10 per cent. of acetic acid, is added, an abundant white flocculent precipitate is formed; this is collected, and purified by re-solution and reprecipitation by dilute alkali and acid respectively. It gives no reduction with Trommer's test; but after boiling for half an hour with 1—2 per cent. hydrochloric, or 2—4 per cent. sulphuric acid, the product gives an abundant reduction. In addition to this reducing substance, there is also a formation of guanine.

The glucoproteïds, like the mucins and the mucoids, contain less nitrogen (6 to 13 per cent.) than simple proteïds. The present substance, however, has the high percentage of 17·4 of nitrogen. The obtaining of guanine, moreover, suggested the explanation that the substance in question is a nuclein-like material. The guanine is not simply a mechanical mixture; because no guanine can be obtained from it unless it is previously treated with a mineral acid, and, moreover, elementary analysis of eight preparations gave very concordant results. The mean of the analyses quoted gives C, 43·62; H, 5·45; N, 17·39; S, 0·728; P, 4·48 per cent. There is a very noteworthy percentage of phosphorus. On subjecting it to gastric digestion, the residual nuclein was found to contain 5·21 per cent. of phosphorus. The amounts of phosphorus in the proteïds and in its nuclein constituent are thus fairly close, and the solubilities of the substance are like those of the nucleïns. It is termed a nucleo-proteïd. The occurrence of a reducing sugar-like substance from nuclein is not unique, as Kossel and his pupils have obtained similar results with yeast-nuclein. This sugar, if such it be, does not ferment with yeast;

like the pentoses, it gives a reaction with phloroglucinol and hydrochloric acid, and by distillation with hydrochloric acid yields furfuraldehyde. It was not, however, obtained in a pure condition. An osazone, partly crystalline, partly amorphous, was obtained; the latter becoming crystalline after repeated recrystallisations. The crystals were fine needles grouped in rosettes; their melting point was 158—160°. Its properties are not identical with those of any known osazone, and no elementary analysis was made. It appears to be most like the osazones prepared from pentaglucofoses by E. Salkowski and M. Jastrowitz (*Cent. med. Wiss.*, 1892, Nos. 19 and 32). The possibility that it may contain two osazones, one of them being that of glycuronic acid, is also suggested. Glycuronic acid gives the reaction for pentoses.

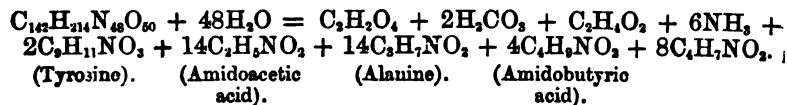
This nucleo-proteid, or phospho-glucoproteid, is the result of the decomposition produced by boiling the proteid in the pancreatic cells, and resembles those which in the case of other organs have received the names of tissue-fibrinogen (Wooldridge), cytoglobulin and präglobulin (Alex. Schmidt), nucleo-albumin (Pekelharing), nucleo-histon (Kossel and Lilienfeld) and several other names. This more complicated nucleo-proteid, the more immediate product of the cells, is split by boiling into coagulated proteid, and the phospho-glucoproteid which is the more immediate subject of this paper. It is further suggested that in the case of the pancreas the more complicated nucleo-proteid is identical with trypsin.

In conclusion, some suggestions regarding nomenclature are made:—

The term *nuclein* should be restricted to the insoluble residues left after gastric digestion, which consist of compounds of proteid and nucleic acid, and which by further decomposition yield xanthine-like substances. The paranucleins of Kossel which do not yield these so-called nuclein-bases include a number of very different substances (Liebermann's lecithalbumins, the nuclein-like substances from ichthulin which also yield a reducing substance, and that from casein which does not, Liebermann's artificial nuclein) and should be called *pseudo-nucleins*. The term *nucleo-albumin* should be given to substances like casein which yield a pseudo-nuclein, and *nucleo-proteid* to those which yield true nuclein.

W. D. H.

Constitution of Silk. By H. SILBERMANN (*Chem. Zeit.*, 17, 1693—1695).—Crude silk fibre consists of two parts, fibroin the true thread substance, and a gelatinous body which surrounds it and which is termed sericin. On heating fibroin with barium hydroxide under pressure, ammonia, acetic acid, carbonic anhydride, oxalic acid, tyrosine (9·5—10 per cent.) alanine, amidobutyric acid, amidoacetic acid, and an amido-acid with the formula $C_4H_7NO_3$, are formed. The following equation represents the hydrolysis of fibroin,



The author gives a constitutional formula for silk, according to which it contains three principal groups, two derived from carbamide and one from tetramide. He does not consider fibroin a homogeneous substance. In its general reactions, silk behaves like an amido-acid, combining both with basic rosaniline, and with acid azodyes.

J. B. T.

[*Note by Abstractor.*—The molecular weight of fibroin is given in the original paper as 1970, the above formula corresponds to 3390.]

Hæmatin Hydrochloride and Hydrobromide. By W. KÜSTER (*Ber.*, 27, 572—578).—Hæmatin hydrochloride was prepared by Nencki and Seiber's method, both from blood and from oxyhæmoglobin, by the action of amylic alcohol and hydrochloric acid; re-crystallized oxyhæmoglobin from horse blood, on treatment with alcohol (93 per cent.) is dehydrated and the product, called para-hæmoglobin, on treatment with amylic alcohol and hydrochloric acid also yields hæmatin hydrochloride. The author's analyses of the crystalline compound of hæmatin hydrochloride and amylic alcohol point to the formula $(C_{22}H_{30}N_4FeO_3, HCl)_2, C_5H_{12}O$, instead of $(C_{22}H_{30}N_4FeO_3, HCl)_4, C_5H_{12}O$, as given by Nencki, but only in one experiment was it possible to expel the alcohol completely by heating at 130—135°. By the action of hydrogen bromide on hæmatin in absolute ethylic alcoholic solution the compound



is obtained in small, dark coloured, rhombic crystals. The alcohol is eliminated by treatment with soda.

J. B. T.

Organic Chemistry.

Phenomena of Oxidation and Chemical Properties of Gases.

By F. C. PHILLIPS (*Amer. Chem. J.*, 16, 163—187; 235—254).—
See this vol., ii, 293, 294.

Calcium Carbide. By H. MOISSAN (*Compt. rend.*, 118, 501—506).—Calcium carbide is obtained by placing an intimate mixture of 120 grams of calcium oxide from marble and 70 grams of carbon from sugar in the crucible of the electric furnace, and subjecting it to the action of a current of 350 ampères and 70 volts for 15 or 20 minutes. The yield is from 120 to 150 grams.

The carbide has the composition C_2Ca , and forms a fused, homogeneous, black mass, which cleaves easily, and has a distinctly crystalline fracture. The crystals are brilliant and opaque; sp. gr. at $18^\circ = 2.22$. Calcium carbide is insoluble in carbon bisulphide, light petroleum, benzene, and all ordinary reagents. It is not altered when heated in hydrogen gas, not attacked by nitrogen at 1200° , nor by silicon or boron at a bright red heat. It is not attacked by sodium or magnesium at the softening point of glass, nor by tin at a red heat, nor by iron at a dull red heat, but at a higher temperature it yields a carburetted alloy of iron and calcium, and with antimony at a red heat it forms a crystalline alloy containing calcium. Dry chlorine does not attack the carbide in the cold, but at 245° it becomes incandescent, and yields carbon and calcium chloride; bromine behaves similarly at 350° , and iodine at 305° . At a dull red heat, the carbide burns in oxygen, with formation of calcium carbonate, and at 500° it becomes incandescent in sulphur vapour, and yields calcium sulphide and carbon bisulphide.

Calcium carbide rapidly decomposes water, with evolution of almost perfectly pure acetylene and development of heat. When the carbide is heated to dull redness in water vapour, the decomposition is much less rapid, and the gas evolved consists of hydrogen and acetylene. Dilute acids behave in the same way as water, but fuming nitric and sulphuric acid attack it but slightly. Ordinary sulphuric acid, however, attacks it, and an odour of aldehyde is given off. When heated in a current of dry hydrogen chloride, the carbide becomes incandescent, and the gas evolved contains a large proportion of hydrogen.

When calcium carbide is brought into contact with fused chromic anhydride, carbonic anhydride is formed, with incandescence. A solution of chromic acid produces only acetylene. Fused potassium chlorate or nitrate has little action on the carbide, but at a red heat oxidation takes place, with incandescence, and calcium carbonate is formed. Lead peroxide oxidises the carbide, with incandescence, below a red heat, and the reduced lead contains calcium. When triturated with lead chromate at the ordinary temperature, the carbide becomes incandescent. If the carbide is heated with absolute alcohol,

in sealed tubes, at 180° , it yields calcium ethoxide and acetylene, $2\text{EtOH} + \text{C}_2\text{Ca} = \text{C}_2\text{H}_2 + \text{Ca}(\text{OEt})_2$. The acetylene is completely absorbed by ammoniacal cuprous chloride, but the acetylde that is formed is black.

If some fragments of calcium carbide are allowed to fall into water saturated with chlorine, bubbles of acetylene are at once evolved, but take fire in contact with the chlorine, and the odour of carbon chlorides is recognisable.

C. H. B.

Barium and Strontium Carbides. By H. MOISSAN (*Compt. rend.*, 118, 683—686).—*Barium carbide*, BaC_2 , is obtained by heating in a carbon crucible in the electric furnace with a current of 70 vols. and 350 ampères, an intimate mixture of 50 grams of anhydrous barium oxide and 30 grams of carbon from sugar, or a mixture of 150 grams of pure barium carbonate and 25 grams of carbon from sugar. The product is a fused, black, brittle mass, composed of large, lamellar crystals. It is the most fusible of the carbides of the alkali earths; sp. gr. = 3.75.

Strontium carbide, SrC_2 , is obtained in a similar manner with 120 grams of strontium oxide and 30 grams of carbon, or 150 grams of strontium carbonate and 50 grams of carbon. The black product has a lustrous, crystalline fracture; sp. gr. = 3.19.

Both carbides are decomposed by water, with formation of the hydroxides and evolution of pure acetylene. The action of concentrated and dilute acids is the same as with calcium carbide (preceding Abstract). With the gaseous hydracids, the carbide becomes incandescent if the temperature is sufficiently high. The following table gives the temperature of incandescence of the three carbides in various other vapours.

	Dry chlorine.	Bromine.	Iodine.
C_2Ca	245°	350°	305°
C_2Sr	197	174	182
C_2Ba	140	130	122

The action of oxygen is also very energetic, but requires a temperature approaching the softening point of glass; under these conditions the barium carbide becomes vividly incandescent. The barium carbide is decomposed, with incandescence, by sulphur at a temperature somewhat above the melting point of the latter, barium and carbon sulphides being formed. At 500° , strontium carbide is decomposed in a similar manner. Selenium decomposes both compounds, with incandescence, producing carbon selenide and a metallic selenide. Silicon and boron have no action at 1000° ; nitrogen has no apparent effect, but if the residue is treated with boiling water, after evolution of acetylene, some ammonia is evolved. At a dull red heat, phosphorus produces brilliant incandescence, with formation of a phosphide; arsenic acts with less energy, and requires a higher temperature.

C. H. B.

Hydrophosphocyanic acid. By W. B. SHOBER and F. W. SPANUTIUS (*Amer. Chem. J.*, 16, 229—232).—Sodium, free from oxide

and hydroxide, was introduced into a hard, glass tube, and melted in a current of pure, dry hydrogen. When the sodium was fused, the hydrogen current was replaced by a slow current of pure and dry phosphine, the sodium being kept strongly heated. The sodium was gradually converted into a black mass, which was either PH_3Na , PHNa_2 , or PNa_3 , or a mixture of these. Without allowing the apparatus to cool, the phosphine current was then replaced by pure, dry, carbonic oxide, and this passed for an hour. The mass so produced was spontaneously inflammable in air, and was decomposed by water, with evolution of phosphine. Treated with alcohol, a part dissolved, leaving a black residue, but the solution gradually decomposed. It was found impossible to isolate any of the products. When treated with alkalis, the product yields phosphine and formic acid, from which the authors conclude that it contained *hydrophosphocyanic acid*, HCP, the analogue of hydrocyanic acid. The authors hope to investigate this reaction further.

L. T. T.

Preparation of Pentadecylic Alcohol from Palmitic acid.

By L. PANIC (Monatsh., 15, 9—16).—The author has prepared pentadecylic alcohol from palmitic acid, by first treating the silver salt with iodine, and then converting the salt, $\text{C}_{15}\text{H}_{31}\cdot\text{COOC}_{15}\text{H}_{31}$, thus obtained into the alcohol, $\text{C}_{15}\text{H}_{31}\cdot\text{OH}$ (compare Simonini, Abstr., 1892, 1301; 1893, i, 391). *Pentadecylic bromide*, $\text{C}_{15}\text{H}_{31}\cdot\text{Br}$, obtained on heating the alcohol with concentrated hydrobromic acid, at 120° , in sealed tubes, is a brownish oil, which may be solidified by cold, and then melts at $14\text{--}15^\circ$. On treatment with alcoholic potassium cyanide, and subsequent hydrolysis, it yielded traces of palmitic acid. *Pentadecylic acetate*, $\text{C}_{15}\text{H}_{31}\cdot\text{OAc}$, is obtained on heating the alcohol with a large excess of acetic anhydride, in sealed tubes for 20 hours, at 200° . It boils at 230° , under a pressure of 70 mm., has an ethereal odour, and, when strongly cooled, forms a wax-like mass, which melts at $10\text{--}11^\circ$. On oxidation, the alcohol is converted into pentadecioic acid, $\text{C}_{15}\text{H}_{31}\cdot\text{COOH}$, which is obtained in the form of a white mass, having a mother-of-pearl lustre. This melts at 50° , yields an amorphous, white silver salt, and appears to be identical with the acid (m. p. 51°) obtained from methyl pentadecyl ketone by Krafft (Abstr., 1880, 34).

G. T. M.

Compounds of Amidoguanidine and Sugars. By H. WOLFF (Ber., 27, 971—974).—*Glucosamidoguanidine hydrochloride*,



is prepared by the interaction of amidoguanidine hydrochloride and glucose (dextrose) in alcoholic solution; it is deposited in rhombic crystals, and, when dried, melts at 165° . The specific rotatory power $[\alpha]_D = -8.94$. On treatment with dilute hydrochloric acid, the compound is hydrolysed, but the action is incomplete. The *sulphate* crystallises in thin plates, the *acetate* in needles; both are *laevogyrate*. The *hydrogen sulphate* is liquid; and the *nitrate* crystallises in needles melting at 180° . The *hexacetyl derivative*, $\text{C}_6\text{H}_{11}\text{N}_4\text{O}_5\text{Ac}_6$,

z 2

+ H_2O , is crystalline, and lævogyrate; five acetyl groups are eliminated by the action of acids or alkalis, and the product, $\text{C}_9\text{H}_{16}\text{N}_4\text{O}_6 + 2\text{H}_2\text{O}$, is deposited from water in rhombic crystals; it is dextrogyrate, and has a slightly sweet taste. It is a derivative of dicyanogen, containing the group $\begin{array}{c} \text{NH}:\text{C}:\text{N}:\text{N}:\text{R} \\ | \quad | \\ \text{N}:\text{C}:\text{Me} \end{array}$ formed from the acetyl compound $\text{NH}:\text{C}(\text{NHAc})\cdot\text{NH}\cdot\text{N}:\text{R}$, and is stable towards acids and alkalis. J. B. T.

Yeast-gum. By E. SALKOWSKI (*Ber.*, 27, 925—926; compare this vol., i, 222).—Since the publication of the paper referred to above, the author has become acquainted with a paper on the same subject published by Hessenland, in the *Zeit. Vereins Rübenzuck-Ind.*, 1892, 671. Hessenland finds that the composition of yeast-gum is expressed by the formula $\text{C}_8\text{H}_{10}\text{O}_8$, whereas according to the author it is $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (substance dried at 110°). Hessenland finds that on hydrolysis, *d*-mannose, accompanied by a little dextrose, is formed. The author considers that this seems to show that yeast-gum, at all events, when prepared by the process used by Hessenland, is a mixture of compounds. A. H.

Action of Nitric acid on Aldehydes and Ketones. By H. APETZ and C. HELL (*Ber.*, 27, 933—948; compare *Ber.*, 14, 979).—Nitric acid acts on methyl hexyl ketone and on acetophenone with the production of a small amount of a nitrile, whilst no substance of this class is formed when benzaldehyde or furfuraldehyde is thus treated. The action of the acid on acetone is of a complicated character, and has also been investigated by Behrend and Schmidt (*Abstr.*, 1893, i, 303). When acetone is slowly added to cooled fuming nitric acid, a violent action occurs, and an oil is formed, probably a mixture; when this is treated with ammonia, it yields a substance, probably $\text{C}_{24}\text{H}_{22}\text{N}_{18}\text{O}_6$, which crystallises in thin scales of a greyish-yellow colour, and characteristic lustre. When treated with acetic chloride, it yields an *acetyl*-derivative of the formula $\text{C}_{24}\text{H}_{22}\text{N}_{18}\text{O}_6\text{Ac}_2$, which crystallises from alcohol in large, yellowish-white, silky needles melting at 164 — 165° . It was found impossible to regenerate the original substance by the hydrolysis of this *acetyl*-derivative. The *benzoyl*-derivative, $\text{C}_{24}\text{H}_{18}\text{N}_{18}\text{O}_6\text{Bz}_2$, forms small, yellowish-white needles, melting at 193 — 195° . A *nitro*-derivative can also be obtained, which, like the benzoyl compound, contains three acid groups. It forms long, yellowish-white needles, which decompose with evolution of gas when heated. The compound $\text{C}_{24}\text{H}_{22}\text{N}_{18}\text{O}_6$ also yields a bromo-derivative, which forms microscopic, yellow crystals, and appears to have the formula $\text{C}_{24}\text{H}_{14}\text{N}_{18}\text{O}_6\text{Br}_6$.

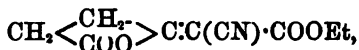
When the compound $\text{C}_{24}\text{H}_{22}\text{N}_{18}\text{O}_6$ is oxidised with potassium permanganate solution, an acid of the formula $\text{C}_8\text{H}_8\text{N}_6\text{O}_6$ is formed, which is being further investigated.

The authors are of opinion that the oil obtained by the action of nitric acid on acetone contains a compound, $\text{COMe}\cdot\text{C}(\text{OH})\cdot\text{NOH}$, from which the crystalline substance of the formula $\text{C}_{24}\text{H}_{22}\text{N}_{18}\text{O}_6$ is

obtained by the addition of the elements of ammonia and the elimination of the elements of water.

A. H.

Derivatives of Ethereal Salts of Cyanacetic acid. By P. T. MULLER (*Ann. Chim. Phys.*, [7], 1, 463—547).—By boiling succinic chloride with ethylic sodiocyanacetate in presence of ether, or by mixing the reagents in presence of benzene at the ordinary temperature, there are formed ethylic succinocyanacetate,



melting at 125—126° (see Abstr., 1891, 1337), and ethylic succinodicyanacetate (Abstr., 1893, i, 143).

If ethylic sodiocyanacetate is boiled with phthalic chloride, two isomeric ethylic phthalocyanacetates are formed (Abstr., 1893, i, 467). When the reaction takes place at the ordinary temperature, a third compound, *ethylic phthalodicyanacetate*, is also formed. It has probably the constitution $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{C}:\text{C}(\text{CN})\cdot\text{COOEt}$, and melts at 158—160°.

Ethylic isonitrosocyanacetate (Abstr., 1891, 1450) melts at 128—129°; two molecular proportions of it combine with one of certain amines, forming compounds which are resolved into the base and isonitrosocyanacetic acid by alkalis. The compounds formed with aniline, orthotoluidine, and paratoluidine, melt at 91—92°, 95°, and 93—94° respectively. When the ethylic salt just described is boiled with ethylic iodide and sodium ethoxide, it is further ethylated, and gives rise to the compound $\text{COOEt}\cdot\text{C}(\text{CN})\cdot\text{NOEt}$, which boils at 125—127° under a pressure of 22—24 mm. Potassium isonitrosomalonnate (Baeyer, *Annalen*, 131, 295) is obtained when ethylic isonitrosocyanacetate is boiled with 33 per cent. potash; whilst isonitrosocyanacetic acid (Wolff and Gans, Abstr., 1891, 897; Söderbaum, *ibid.*, 1184) is formed when the ethylic salt is heated with 7 per cent. soda at 55—60°. When ethylic isonitrosocyanacetate is treated with alcoholic hydrogen chloride, ethylic isonitrosomalonnate (Conrad and Bischoff, *Annalen*, 209, 211) is formed.

Methylic isonitrosocyanacetate (Abstr., 1891, 1450) melts at 119—120°; it crystallises from water with 1H₂O, the hydrated compound melting at 60—65°. When ethylated, it yields the compound $\text{COOMe}\cdot\text{C}(\text{CN})\cdot\text{NOEt}$, which boils at 121—124° under a pressure of 23—25 mm. The *benzoyl* derivative, $\text{COOMe}\cdot\text{C}(\text{CN})\cdot\text{NOBz}$, melts at 131—132°. Methylic isonitrosocyanacetate yields methylic isonitrosomalonnate when treated with alcoholic hydrogen chloride; this melts at 66—67°.

When ethylic fumarate is heated with ethylic sodiocyanacetate in alcoholic solution, and the product boiled with dilute sulphuric acid, ethylic α -cyanotricarballylate is obtained, which, on hydrolysis with hydrochloric acid, yields the corresponding acid (Simpson, *Annalen*, 128, 353). Ethylic citraconate reacts in a similar manner with ethylic sodiocyanacetate (see also Abstr., 1892, 1181).

A. R. L.

β -Dibromopropionic acid. By R. THOMAS-MAMEET (*Compt. rend.*, 118, 652—653).— β -Dibromopropionic acid, $\text{CHBr}_2\cdot\text{CH}_2\cdot\text{COOH}$, is obtained by heating β -bromacrylic acid, $\text{CHBr}\cdot\text{CH}\cdot\text{COOH}$, in sealed tubes at 100° with fuming hydrobromic acid. The product is dissolved in benzene, decolorised by means of animal charcoal, and allowed to crystallise. It forms long, rhombic prisms, which melt at 71° (uncorr.). The crystals always show the faces p' and the facettes e' , sometimes together with the faces h' or a' . They show the combinations $p\ e'\ h'$, and $p\ e'\ a'$, and the angles observed are aa' , $109^\circ 20'$; pe' , $137^\circ 30'$; ee' , 85° ; pa' , $109^\circ 27'$. The ratios of the axes $a : b : c = 0.649 : 1 : 0.916$.

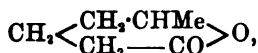
When the acid is treated with alcoholic potash, β -bromacrylic acid is obtained, melting at 115° .
C. H. B.

Isocaproic acid and the Solubilities of its Calcium, Barium, and Silver Salts. By J. KÖNIG (*Monatsh.*, 15, 17—27).—As contradictory statements have been published regarding the barium and calcium salts of this acid, the author has considered it desirable to synthesise them from pure materials. The method adopted was to prepare ethylic isobutylmalonate, $\text{C}_{11}\text{H}_{20}\text{O}_4$, which boils at 225 — 226° , by gradually adding sodium ethoxide in alcoholic solution to a mixture of isobutylic iodide and ethylic malonate. From this the free acid $\text{C}_7\text{H}_{12}\text{O}_4$, which forms drusy masses of crystals, and melts at 107° , was obtained; and this, on heating in a reflux apparatus, was resolved into carbonic anhydride and *isobutylic acid*. The latter boils at 197 — 198° , and furnishes the following salts. The *calcium salt*, $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_2)_2 + 5\text{H}_2\text{O}$, crystallises in slender needles, and has the solubility $s = 7.38 - 0.12402(t - 0.8) + 0.00182(t - 0.8)^2$. The *barium salt*, $(\text{C}_6\text{H}_{11}\text{O}_2)_2\text{Ba} + 4\text{H}_2\text{O}$, crystallises in needles resembling the calcium salt, and has the solubility $s = 14.28 - 0.11648(t - 0.5) + 0.00176(t - 0.5)^2$. The *silver salt* forms groups of feathery crystals, and has the solubility $s = 0.1674 - 0.000849(t - 1) + 0.0000322(t - 1)^2$.
G T. M.

Stereoisomeric α -Methyl- β -chlorocrotonic acids. By R. OTTO (*Ber.*, 27, 948—949; compare *Abstr.*, 1890, 957). When dichlorodimethylsuccinic acid is heated with water at 120 — 130° , both of the isomeric chlorotiglic acids (melting at 73° and 55°) are formed, and not merely the derivatives of higher melting point, as formerly stated.

A. H.

Derivatives of δ -Hydroxycaproic acid. By J. ZELLNER (*Monatsh.*, 15, 29—36).—The starting point of this investigation was Wolff's lactone of normal δ -hydroxycaproic acid,



(*Annalen*, 216, 128), which was dissolved in 10 times its weight of phosphorus oxychloride, and heated in a water bath for two hours with a molecular equivalent of phosphorus pentachloride. On distilling off the phosphorus oxychloride in a vacuum, and boiling the resulting chloride of δ -chlorocaproic acid with alcohol, *ethylic*

δ-chlorocaproate, $C_6H_{11}ClO_2$, was obtained. This substance boils, with slight decomposition, at $217-221^\circ$, is insoluble in water, dissolves in alcohol and ether, has a peculiar fruity smell, and a sp. gr. 1.04 at 20° . On heating with potassium phthalimide at 180° , it is resolved into a mixture of hydrochloric acid and the ethylic salt of an unsaturated acid, $C_6H_{11}O_2$; and, on heating with alcoholic ammonia at $160-170^\circ$, it is converted into a yellow, syrupy compound which is most probably α -methyl- α -piperidone, for, on distillation with zinc dust, it gives rise to α -pipercoline. G. T. M.

Substituted Crotonolactones and Mucobromic acid. By H. B. HILL and R. W. CORNELISON (*Amer. Chem. J.*, **16**, 188-213).—In 1890, Hill and Jackson (*Abstr.*, 1890, 600), by the action of hydrochloric acid on $\beta\delta$ -dichloropyromucic acid, obtained a compound $C_4H_5ClO_2$ (melting at $52-53^\circ$), and Hill and Sanger (*Proc. Amer. Acad.*, **21**, 158) obtained a similar compound $C_4H_5BrO_2$ (melting at 77°) amongst the products of the action of soda on pyromucic tetrabromide. The authors have studied these and analogous reactions.

β -Bromocrotonolactone, $C_4H_5BrO_2$, is formed, with evolution of carbonic anhydride, when $\beta\delta$ -dibromopyromucic acid is boiled with concentrated hydrobromic acid, and also by the partial reduction of $\alpha\beta$ -dibromocrotonolactone. It melts at 58° , boils under 18 mm. pressure at 140° , and distils with steam. It crystallises in hexagonal plates or truncated prisms, is readily soluble in boiling water, alcohol, and benzene, sparingly in light petroleum. Alkalis cause the separation of alkali bromides, whilst aniline appears to form a substitution derivative which, however, could not be isolated. Bromine, in the cold, forms an additive product, tribromobutyrolactone, $C_4H_3Br_3O_2$, which crystallises in brilliant prisms melting at $63-64^\circ$. At 100° , bromine forms mucobromyl bromide; no characteristic oxidation products could be obtained.

$\alpha\beta$ -Dibromocrotonolactone, $C_4H_3Br_2O_2$, is formed, with evolution of carbonic anhydride, when tribromopyromucic acid is heated at 130° with dilute sulphuric acid (sp. gr. 1.43), or boiled with concentrated hydrobromic acid. It crystallises in six-sided plates or in prisms, is sparingly soluble in cold alcohol, ether, light petroleum, or water, easily so in benzene or chloroform. It melts at $90-91^\circ$, boils under 18 mm. pressure at 145° , and distils rapidly with steam. It is very stable towards acids, but unstable towards alkalis, in which it dissolves with formation of alkali bromides, yielding a yellow solution. When dilute potash is employed, 2 mols. of the latter are neutralised, whilst only 1 mol. of potassium bromide is formed, thus leaving but little doubt of its lactonic structure. It is converted into mucobromic acid by boiling with bromine and water. It may be crystallised unchanged from strong nitric acid, but by long boiling with the latter is converted into mucobromic and dibromomaleic acids. It does not combine with hydrogen sodium sulphite, whilst aniline and phenylhydrazine both remove bromine from it. When treated with zinc and dilute sulphuric acid, a lactone of hydroxycrotonic acid is formed, thus establishing its structure.

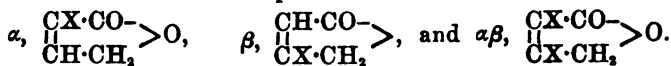
When digested with bromine water, the lactone is slowly converted

into mucobromic acid, the oxidation being much hastened by using concentrated hydrobromic acid as the solvent for the bromine. Chromic acid and silver oxide cause more complete oxidation, carbonic anhydride being evolved, and only traces of mucobromic and dibromomaleic acids formed.

This compound is identical with that erroneously described by Toennies (Abstr., 1879, 918) as dibromofumaric aldehyde. It may also be produced by acting on phosphorus dissolved in carbon bisulphide with an intimate mixture of equivalent weights of iodine and mucobromic acid, or by the reduction of mucobromyl bromide. Bromine does not act on the lactone in the cold, but at 100°, 1 mol. prop. of bromine produces mucobromyl bromide, whilst with excess of bromine, *unsymmetrical dibromomaleic bromide*, $C_4Br_2O_3$, is formed. The latter crystallises from light petroleum in leaflets which are extremely soluble in alcohol, ether, chloroform, benzene, and carbon bisulphide, more sparingly in light petroleum; it has a strong, suffocating odour like that of the acid dibromanhydrides, and melts at 58—59°. When heated with water, it is slowly converted into dibromomaleic acid. The authors have as yet been unable to obtain either this compound or an isomeride from dibromomaleic acid. When the lactone is treated with aniline, aniline bromide is separated and α -phenylamido- β -bromocrotonolactone formed. This crystallises in needles or plates; if quickly heated, it melts at 186—187°; if slowly, it decomposes and melts about 165°. It is easily soluble in boiling glacial acetic acid, sparingly in the other organic solvents, and in water.

It dissolves in warm alkalis, and is deposited unchanged if the solution is cooled rapidly; but if the solution is kept warm, decomposition takes place with formation of phenylic isocyanide. α -Iodo- β -bromocrotonolactone is formed from the dibromolactone by the action of aqueous hydriodic acid; it forms colourless prisms, colours on exposure to air, and melts at 119—120°; it resembles the dibromoderivative in its properties. Hydriodic acid causes the separation of iodine, and the formation of a viscous, oily substance, but the products could not be isolated. With aniline, it yields α -phenylamido- β -bromocrotonolactone already described, and, on reduction with zinc dust, β -bromocrotonolactone.

The authors consider that the results of their investigations establish for the lactones the respective formulæ



L. T. T.

Substituted Crotonolactones and Mucobromic acid. By H. B. HILL and R. W. CORNELISON (*Amer. Chem. J.*, 16, 277—307; compare preceding abstract).— α -Bromocrotonolactone, $C_4H_3BrO_2$, prepared by the action of zinc dust and acetic acid on bromomaleic bromide, is also formed by the action of bromine on β -bromopyromucic acid in aqueous solution. It crystallises in long, transparent prisms, melts at 77°, and dissolves freely in boiling water, alcohol, and chloroform, but only sparingly in carbon bisulphide, ether,

benzene, and light petroleum. Bromine converts it into $\alpha\beta$ -dibromocrotonolactone and mucobromic bromide; but when oxidised by bromine water, it yields mucobromic acid and much carbonic anhydride (compare Hill and Sanger, *Proc. Amer. Acad.*, **21**, 158; *Abstr.*, 1884, 1305). α -Phenylamidocrotonolactone is obtained by the interaction of α -bromocrotonolactone and aniline, also by reducing α -phenylamido- β -bromocrotonolactone with sodium amalgam in alcohol. It crystallises in aggregates of needles, melts at $217-218^\circ$, and dissolves readily in boiling alcohol and in hot glacial acetic acid, sparingly in boiling water, hot benzene, or chloroform, and scarcely at all in ether, light petroleum, and carbon bisulphide.

$\alpha\beta$ -Dibromocrotonolactone is reduced to crotonolactone by zinc and dilute sulphuric acid at 100° .

Mucochloric bromide, $C_4HCl_2O_2Br$, prepared by the action of phosphorous bromide on mucochloric acid, crystallises in large, transparent plates, melts at 86° , and dissolves readily in alcohol, ether, chloroform, carbon bisulphide, and benzene, but more sparingly in light petroleum. Its alcoholic solution gives a transient, deep purple colour with alkalis.

$\alpha\beta$ -Dichlorocrotonolactone, $C_4H_2Cl_2O_2$, is the product obtained by reducing mucochloric bromide by stannous chloride in hydrochloric acid; it crystallises in long, silky needles or in six-sided plates, melts at $50-51^\circ$, boils at $114-115^\circ$ (18 mm.), and dissolves in boiling water, benzene, chloroform, alcohol, ether, and, more sparingly, in carbon bisulphide. It yields mucochloric acid on oxidation. With aniline, it forms α -phenylamido- β -crotonolactone, which crystallises in flat prisms, melts at 183° , and dissolves freely in boiling alcohol and boiling chloroform, more sparingly in carbon bisulphide, but not at all in light petroleum. Hydriodic acid converts $\alpha\beta$ -dichlorocrotonolactone into α -iodo- β -chlorocrotonolactone; this crystallises in long, flat needles, melts at $108-109^\circ$, and dissolves in hot alcohol, benzene, or ether, and, more sparingly, in chloroform and carbon bisulphide.

β -Chlorocrotonolactone is prepared by reducing $\alpha\beta$ -dichlorocrotonolactone by zinc dust in acetic acid; it crystallises in flat prisms, melts at $25-26^\circ$, boils at $124-125^\circ$ (18 mm.), and dissolves in hot water, alcohol, ether, chloroform, and benzene, but only sparingly in light petroleum. It is also formed when $\beta\delta$ -dichloropyromucic acid is heated with acids.

Mucophenoxybromic bromide, $OPh \cdot C_4H_2BrO_2$, produced by the action of phosphorous bromide on mucophenoxybromic acid (*Proc. Amer. Acad.*, **21**, 262; *Abstr.*, 1884, 731), crystallises in needles, melts at $95-96^\circ$, and dissolves readily in ether, chloroform, benzene, and hot alcohol, but only sparingly in light petroleum. It is easily reduced to α -phenoxy- β -bromocrotonolactone, which is crystalline, and is soluble in ether, chloroform, benzene, glacial acetic acid, and hot alcohol.

When the last-named lactone is dissolved in a hot solution of potassium hydroxide and excess of hydrochloric acid is added, α -phenoxy- β -bromo- γ -hydroxycrotonic acid crystallises out; it forms flat, rectangular prisms, with $1H_2O$, melts at about 98° , and dissolves in

alcohol, ether, hot chloroform, and in benzene, but not in light petroleum; the *barium* salt, with $3\text{H}_2\text{O}$, is soluble in water.

Mucophenoxychloric bromide crystallises in stellate needles, melts at $89-90^\circ$, and dissolves freely in hot alcohol. When reduced, it yields *α -phenoxy- β -chlorocrotonolactone*, which crystallises in six-sided plates or flat prisms, melts at $67-68^\circ$, and dissolves in ether, chloroform, benzene, carbon bisulphide, hot alcohol, and light petroleum, but not in water. By alkalis it is converted into *α -phenoxy- β -chloro- η -hydroxycrotonic acid*; this crystallises in flat, rectangular prisms with $1\text{H}_2\text{O}$, melts at about 76° , and dissolves readily in alcohol, ether, chloroform, and benzene, less freely in carbon bisulphide and light petroleum, but only sparingly in water, which, when hot, converts it into the lactone; the *barium* salt, with $3\text{H}_2\text{O}$, is soluble in water.

Mucobromoxime, $\text{C}_4\text{H}_5\text{Br}_2\text{NO}_2$, obtained by the interaction of mucobromic acid and hydroxylamine in alkaline solution, is a granular precipitate without definite melting point; it dissolves in alcohol, ether, and boiling water. When allowed to stand in the liquid from which it is precipitated, it rapidly changes into its *anhydride*, $\text{C}_4\text{HBr}_2\text{NO}_2$, which crystallises in dendritic needles, melts about $117-118^\circ$, and dissolves in alcohol, chloroform, and benzene; when heated above its melting point, it changes into its isomeride, dibromomaleinimide (Abstr., 1884, 1115); when heated with water, it yields hydrogen ammonium dibromomaleate. The *methyl* derivative of mucobromoxime, $\text{C}_4\text{H}_5\text{Br}_2\text{NO}_2\text{Me}$, is obtained by the reaction between hydroxylamine, mucobromic acid, and boiling methylic alcohol; it crystallises in felted needles, melts at $146-147^\circ$, and dissolves in alcohol and hot water, but only sparingly in chloroform, benzene, and cold water.

Mucobromamide, $\text{C}_4\text{HBr}_2\text{O}_2\cdot\text{NH}_3$, is produced when ammonia is passed into an ethereal solution of ethylic mucobromate. It crystallises in colourless, dendritic needles, melts, with decomposition, at about 170° , and dissolves readily in hot alcohol.

By reactions analogous to those just described, there were obtained: *Mucochloroxime*, crystallising in felted needles, melting about 90° , and soluble in alcohol and ether; the *methyl*-derivative of mucochloroxime, crystallising in flat needles, melting, when quickly heated, at 135° , and soluble in alcohol, ether, and chloroform; *mucochloramide*, crystallising in oblique prisms, melting at 166° , and soluble in alcohol and hot water; *mucophenoxybromoxime*, crystallising in long needles, melting at $120-135^\circ$, and soluble in alcohol and in ether; and *mucophenoxychloroxime*, crystallising in aggregates of needles, melting at $112-125^\circ$, and soluble in alcohol and in ether.

A. G. B.

cis-Glutaconic acid. By E. BUCHNER (*Ber.*, 27, 881-883).—A comparison of the glutaconic acid prepared from methylic pyrazolone-3:5-dicarboxylate (*Ber.*, 23, 703), and that from chloroform and sodium malonate, proves the identity of the two preparations. The pure acid when heated rapidly melts at 138° ; under other conditions at $136-137^\circ$; and, when slowly heated, at 134° . The acid is *cis*-glutaconic acid, seeing that when heated with acetic chloride it is converted

into an anhydride which with soda yields the sodium salt of the original acid. When heated at 100° , a cherry-red coloration is produced. A stereoisomeride could not be prepared by heating it with hydrochloric or hydrobromic acid, and the acid remains unchanged. When melted with potassium hydroxide, it is decomposed, with the production of malonic acid, a part of the latter being also decomposed into acetic acid. The *anhydride* crystallises in flat, pale yellow needles, and melts at 87° .

E. C. R.

Elimination of Carbonic Oxide from Ethylic Oxalacetate and its Derivatives. By W. WISLIZENUS (*Ber.*, 27, 792—798).—When ethylic oxalacetate, or a derivative of it, is heated at 150 — 190° , or distilled under ordinary pressure, it loses carbonic oxide and yields ethylic malonate, or a derivative, $\text{COOEt}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOEt} = \text{CO} + \text{CH}_2(\text{COOEt})_2$. This reaction, which it is proposed to term “carbon monoxide elimination” (“Kohlenoxydspaltung”), is the main one in the case of the derivatives, but with ethylic oxalacetate itself other reactions take place in addition. Some condenses forming products of higher boiling point, and some reacts with the water thus formed, yielding carbonic anhydride and ethylic pyruvate, $\text{COOEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOEt} + \text{H}_2\text{O} = \text{CO}_2 + \text{EtOH} + \text{CH}_3\cdot\text{CO}\cdot\text{COOEt}$.

Ethylic oxalacetate, methylloxalacetate, and oxalosuccinate have been found to undergo the above-mentioned change, yielding respectively ethylic malonate, ethylic methylmalonate (isosuccinate), and *ethylic ethenyltricarboxylate*, $\text{COOEt}\cdot\text{CH}_2\cdot\text{CH}(\text{COOEt})_2$. The last substance boils at 276° (uncorr.; at 152 — 153° under 14 mm. pressure). The *acid* itself melts at 159° . Its *sodium salt* and *barium salt*, with H_2O , were prepared. When heated, it decomposes into carbonic anhydride and succinic acid.

C. F. B.

Decomposition of Tartaric and Citric acids by Sunlight. By W. SEEKAMP (*Annalen*, 278, 373—374).—A 5 per cent. solution of tartaric acid, in which 1 per cent. of uranic oxide was dissolved, was exposed to sunlight. Gas was soon evolved, and the liquid became green, due to the reduction of the uranic oxide. After a month, the liquid was examined, and found to contain aldehyde, which was removed by distillation. The residual liquid, which had an acid reaction, was neutralised with lead hydroxide, and from the resulting precipitate, on decomposition with hydrogen sulphide, tartaric, malic, and succinic acids were obtained, whilst the filtrate contained a cupric reducing substance, together with, perhaps, propionic acid. Citric acid behaved in a similar manner.

A. R. L.

Dissociation of Potassium Hydrogen Tartrate. By A. A. NOYES (*Zeit. physikal. Chem.*, 13, 417—418).—The dissociation was determined by the inversion of sugar, according to Trevor's method (*ibid.*, 10, 321), a platinum tube being employed, and the rate of inversion compared with that induced by acetic acid. The reaction constant of a 0.0351 solution of potassium hydrogen tartrate was 0.00422; that of a 0.00785 solution of acetic acid was 0.00463; whence if x is the degree of dissociation of the hydrogen atom of the salt, and α that of the acid, $0.00785 \alpha : 0.0351 x =$

0.00467 : 0.00422. For the dilution employed, $\alpha = 4.67$ per cent., whence $x = 0.944$ per cent., and the value for the dissociation constant of the acid ions $\text{H}\cdot\text{C}_4\text{H}_4\text{O}_6$, is 0.00012. From these numbers, the author deduces the composition of the solution of the salt, which he calculates to contain about 8 per cent. of free undissociated acid.

L. M. J.

Solubility of Potassium Hydrogen Tartrate. By A. A. NOYES and A. A. CLEMENT (*Zeit. physikal. Chem.*, 13, 412—416).—The influence of several salts on the solubility of potassium hydrogen tartrate was investigated. The salts used were the chloride, chlorate, bromide, iodide, nitrate, acetate, and sulphate of potassium. Blarez's conclusion that potassium salts in equivalent amounts have equal effects in lowering the solubility appears to be only a first approximation. The authors' experiments show that the three haloïds have equal effect; the nitrate has a somewhat smaller effect, the chlorate smaller still, and the sulphate the least of all the salts examined. Acetic acid causes an increase in the solubility. This is explained by the fact that the acetic acid is only slightly dissociated, so that the hydrogen ions from the acid tartrate unite with the acetic acid ions to form undissociated acetic acid. The small effect of potassium sulphate is similarly explained, sulphuric acid being only moderately dissociated. The solubility of the salt is also increased by hydrogen chloride or salts of sodium, owing, in the latter case, to the formation of undissociated sodium salts.

L. M. J.

A Cyclic Analogue of Ethylic Ketipate. By W. DIECKMANN (*Ber.*, 27, 965—966).—Ethylic suberate, like ethylic pimelate, is converted into a β -ketonic acid by the action of sodium (this vol., i, 173), but ethylic glutarate and ethylic sebate do not react. That this is due to the arrangement of the atoms in space is shown by the production of ethylic 1:2-diketopentamethylene-3:5-dicarboxylate, $\text{CH}_2 < \begin{matrix} \text{CH}(\text{COOEt}) \cdot \text{CO} \\ \text{CH}(\text{COOEt}) \cdot \text{CO} \end{matrix}$, by the interaction of sodium, ethylic glutarate, and ethylic oxalate, at 120° . It crystallises from alcohol in pale yellow, lustrous needles, from ether in broad, highly refractive prisms, melts at 118° , gives a red coloration with ferric chloride in alcoholic solution, and is completely analogous to ethylic ketipate from ethylic oxalate and ethylic acetate. The sodium salt is yellow and crystalline.

J. B. T.

Reduction of Ethylic Diazoacetate. By R. JAY and T. CURTIUS (*Ber.*, 27, 775—778).—Precise practical details are given for the preparation of hydrazine hydrate from chloroacetic acid; for these the paper must be consulted. When ethylic diazoacetate, $\text{N}_2\cdot\text{CH}\cdot\text{COOEt}$, is reduced with ferrous hydroxide in a feebly alkaline solution, *hydrazineacetic acid*, $\text{N}_2\text{H}_2\cdot\text{CH}\cdot\text{COOH}$, is formed, and not hydrazineacetic acid, $\text{NH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$, which has not yet been obtained. When the solution is acidified, hydrazine and glyoxylic acid are formed. Silver hydrazineacetate was prepared.

C. F. B.

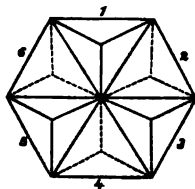
C. F. B.

Acid.	<i>k</i> .
S(CH ₂ .COOH) ₂	0·049
S(CHMe·COOH) ₂ (m. p. 125°)	0·049
(m. p. 109°)	0·044
S(CH ₂ .CH ₂ .COOH) ₂	0·0078
COOH·CH ₂ ·S·CHMe·COOH.....	0·048
COOH·CH ₂ ·S·CH ₂ ·CH ₂ ·COOH.....	0·025
COOH·CH ₂ ·CH ₂ ·S·CHMe·COOH	0·021
S ₂ (CHMe·COOH) ₂	0·090
S ₂ (CH ₂ ·CH ₂ ·COOH) ₂	0·0090
S ₂ (CHMe·COOH) ₂	0·080
SO ₂ (CH ₂ ·COOH) ₂	1·30
SO ₂ (CHMe·COOH) ₂	1·03
SO ₂ (CH ₂ ·CH ₂ ·COOH) ₂	0·024
COOH·CH ₂ ·SO ₂ ·CHMe·COOH	1·24
COOH·CH ₂ ·SO ₂ ·CH ₂ ·CH ₂ ·COOH	0·51

L. M. J.

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figuration of the benzene molecule which does not take cognisance of the difference between the behaviour towards reagents of ortho- and para-derivatives on the one hand, and of meta-derivatives on the other hand, and of the proximity, as it were, of the meta-positions, can correctly represent the constitution of benzene. The author's formula has been already described (Abstr., 1891, 1343), and is expressed by the accompanying figure, in which the continuous and broken lines represent tetrahedra on opposite sides of the plane of the paper.



It is shown that this formula is in accord with Baeyer's investigations on the reduction products of benzene derivatives, and with the fact that meta-derivatives do not tend to form anhydrides.

A. G. B.

Action of Bromine on Paraxylene. By J. ALLAIN LE-CANU (*Compt. rend.*, 118, 534—535).—Tribromo-paraxylene, $C_8H_7Br_3$, is obtained, together with the dibromo-derivative, by the action of bromine on paraxylene in presence of sunlight. It crystallises from ether in rhombic lamellæ, flattened along the base p , and limited by the faces m , h' , the angle of the faces m being very nearly 120° . The crystals are almost always maced along m , and tend towards hexagonal symmetry; they melt at 116° , with some decomposition. When hydrolysed, the tribromo-derivative yields the aldehyde-alcohol, $CHO \cdot C_6H_4 \cdot CH_2 \cdot OH$, a colourless, oily liquid, which is very soluble in ether, and does not boil below 200° . The latter yields a hydrazone, $OH \cdot CH_2 \cdot C_6H_4 \cdot CH \cdot N \cdot NHPh$, a pale yellow powder, which alters rapidly even when not exposed to light, and is only slightly soluble in boiling water.

C. H. B.

Cholesterol. By J. MAUTHNER and W. SUIDA (*Monatsh.*, 15, 85—115).—*Cholestene* (*Hydrocholesterylene*), $C_{27}H_{46}$, may be obtained by reducing cholesterylic chloride, in amylc alcoholic solution, with sodium (compare Walitzky, this Journ., 1877, i, 58). It forms colourless needles, melts at 89 — 90° , and has a rotatory power in chloroform solution of $[\alpha]_D = -56.29^\circ$. When a solution in chloroform is heated with bromine, α - and β -cholestene dibromides, $C_{27}H_{46}Br_2$, are formed. The α -compound crystallises in rhombic prisms, $a : b : c = 0.5456 : 1 : 0.5343$; it melts at 141 — 142° , and rapidly decomposes at a higher temperature. The β -compound crystallises in colourless scales, melts at 106° , and when dissolved in alcohol is slowly converted at ordinary temperatures, or more rapidly, but with partial decomposition, on boiling, into the α -compound. *Cholestene dichloride*, $C_{27}H_{46}Cl_2$, is obtained in a similar manner to the dibromides, and crystallises in scales, which melt at 119 — 120° , an oily substance,

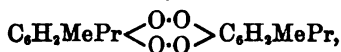
probably an isomeride, being simultaneously formed. All the above-mentioned additive products, on reduction with sodium in amyl alcoholic solution, give cholestene, and not cholestane, $C_{27}H_{48}$, as was expected. *Chlorocholestene dichloride*, $C_{27}H_{46}Cl_2$, is obtained on passing dry chlorine into a solution of cholesterylic chloride in chloroform. It crystallises from a mixture of alcohol and acetone in scales, and melts at 106° . *Cholesterol dichloride*, $C_{27}H_{46}OCl_2 + H_2O$, is formed on passing chlorine into a solution of cholesterol in chloroform. It is anhydrous at 100° , and in that state softens at 125° and melts at 136° . If iodine is present during the absorption, a resinous substance *dichlorocholesterene dichloride*, $C_{27}H_{44}Cl_4O$, is formed in addition to the dichloride described. *Cholesterylic acetate dichloride*, $C_{27}H_{45}Cl_2 \cdot OAc$, may be obtained either by the action of chlorine on cholesterylic acetate, or by warming cholesterol dichloride with acetic anhydride.

On treatment with nitrous acid, cholesterylic chloride is converted into *nitrocholesterylic chloride*, $C_{27}H_{44}Cl \cdot NO_2$, which melts at 149° , and has not the power of directly uniting with bromine. When the nitrous gas was previously passed over calcium chloride, it was found to contain a considerable quantity of chlorine, probably in the form of nitrosyl chloride, and to give rise to the compound $C_{34}H_{58}Cl_2N_2O_3$. This crystallises from its hot solution in glacial acetic acid, in beautiful, long, colourless, needles, melts at 110° , and when heated with an alcoholic solution of potassium acetate is converted into a compound $C_{34}H_{58}Cl_2N_2O_4$, which melts at 147° . By the interaction of cholestene and nitrous acid, a compound was obtained in pale yellow crystals, melting at 105° ; it probably has the composition $C_{27}H_{46}NO_2$, or $C_{27}H_{48}NO_2$, and, like the product from cholesterylic chloride mentioned above, is a fully saturated compound. Endeavours to prepare Preis and Raymann's crystalline dinitrocholesterol, which melts at $120-121^\circ$ (compare Abstr., 1879, 634), were without success, the amorphous product obtained, having the composition $C_{18}H_{27}NO_4$, as shown by the analyses of its dull yellow *silver salt*, $C_{18}H_{26}NO_4Ag$, and bright green *copper salt*, $(C_{18}H_{26}NO_4)_2Cu$.

From their investigations of the cholestene group, the authors conclude, (i) that those compounds, to which cholesterol itself belongs, take up only one molecule of a halogen, and that the saturated hydrocarbon from which they are derived is represented by the formula $C_{27}H_{48}$, and must therefore contain closed chains; (ii) that there exists in the nuclear portions of the compounds at least one asymmetric carbon atom; (iii) that since no halogen acid is eliminated when the compounds are treated with alcoholic potash, the group $\cdot CH \cdot CH \cdot$ is absent, the remarkable stability of the compounds being probably explained by the presence of two directly linked carbon atoms, to each of which two other carbon atoms are immediately attached; (iv) the unknown position taken up by the halogen makes it uncertain whether all the closed chains in the compounds are fully saturated; (v) that the two dibromides described above are probably stereo-isomerides, since one of them is readily converted into the other.

G. T. M.

Constitution of Polythymoquinone. By K. LAGODZINSKI and M. MATEESCU (*Ber.*, 27, 958—961). The formula



given by Liebermann and Ilinski in 1885 to polythymoquinone, is confirmed by the authors' cryoscopic molecular weight determinations, and they suggest that it should be termed dithymoquinone.

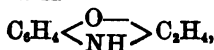
In addition to the phenylhydrazone, benzeneazothymol,



is formed by the interaction of phenylhydrazine and dithymoquinone, being probably produced from the hypothetical thymoquinonephenylhydrazone $\text{NHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_5\text{MePr} \cdot \text{O}$, since thymoquinone and phenylhydrazine hydrochloride yield hydroxythymoquinone and nitrogen. *Benzeneazothymol hydrochloride* is reddish-violet, and undergoes dissociation by prolonged treatment with water. Azophenol and its ethyl ether also form hydrochlorides.

J. B. T.

Orthanisidine. By R. DIEFFENBACH (*Ber.*, 27, 928—933).—This investigation was undertaken with the object of preparing ethylenephenylenediamine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, and phenomorpholine,



(Knorr, *Abstr.*, 1889, 1218) from amidoethylorthanisidine and amidoethylorthamidophenol.

Orthanisidoethylphthalimide, $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, is obtained by the action of orthanisidine on bromethylphthalimide, and forms yellow crystals melting at 118—119°. When it is treated with hydrochloric acid, *amidoethylorthanisidine hydrochloride*,



is obtained in greenish-white crystals, melting at 156°. The free base is a colourless oil, which boils at 277—280°. The *picrate*, $\text{C}_6\text{H}_4\text{N}_2\text{O}_2 \cdot 2\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, separates from alcohol in pale yellow crystals. The base combines with carbon bisulphide to form the corresponding *dithiocarbamate*, $(\text{C}_6\text{H}_4\text{N}_2\text{O})_2\text{CS}_2$, which crystallises in colourless needles, melting at 123°. *Anisidoethylphenylthiocarbamide*,



obtained by the combination of the base with phenylic thiocarbimide, melts at 117—118°. *Dibenzoylamidoethylorthanisidine* forms colourless crystals melting at 134—135°. The free base is not converted by simple heating into ethylenephenylenediamine. *Amidoethylorthamidophenol*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, cannot be obtained from *amidoethylorthanisidine* by treatment with nitrous acid or by heating it with hydrochloric acid, but is formed when it is heated with hydriodic acid, and can be more readily prepared in the same way from *orthanisidoethylphthalimide*. The *hydriodide*, $\text{C}_6\text{H}_4\text{N}_2\text{O} \cdot 2\text{HI} + \text{H}_2\text{O}$, forms colourless crystals, which cannot be recrystallised, and melt at 106—107°. The *sulphate* is almost insoluble in cold water and can

be recrystallised from hot water. The *hydrochloride* separates from amyl alcohol in pale-lilac coloured crystals, which do not melt below 300°. The *picrate* melts at 158—160°. *Tetrabenzoylamidoethylorthamidophenol*, $C_8H_9N_3OBz_4$, forms colourless crystals, melting at 63—65°. The free *amidoethylorthamidophenol* boils at 280—285°, melts at 154—155° and forms colourless crystals. It is not converted by simple heating into phenomorpholine. A. H.

Action of the Salts of Diazobenzene on Methylic and Ethylic Alcohols. By J. L. BEESON (*Amer. Chem. J.*, 16, 235—254).—The decomposition of diazobenzene nitrate with methylic alcohol produces the alkoxy-benzene, whether the change occurs at the ordinary temperature or at the boiling point of the alcohol. Orthonitrophenol, attributed to a molecular rearrangement of the diazobenzene nitrate, is also formed, and is partially converted into 2:4-dinitrophenol by the action of liberated nitric acid. When paranitrophenol is produced it may be traced to the nitration of phenol formed by the action of water, present in the alcohol, on the diazobenzene nitrate.

In the case of the action of diazobenzene nitrate on ethylic alcohol, a high temperature increases the alkoxy-reaction, whilst a low temperature increases the hydrogen reaction (formation of benzene). The presence of a small amount of water increases the alkoxy-reaction.

Excess of alkali or of zinc dust, respectively, brings about the hydrogen reaction (formation of benzene and diphenyl) in the decomposition of diazobenzene nitrate by either alcohol. The same change is produced by the interaction of diazobenzene nitrate with sodium methoxide and ethoxide in solution in their respective alcohols, and in all these three cases there appears to be two reactions, one between the diazo-salt and the neutralising agent, giving the diphenyl reaction, and the other between the diazo-salt and the alcohol giving the hydrogen reaction.

The decomposition of diazobenzene sulphate by methylic alcohol gave nothing but the alkoxy-derivative. A. G. B.

Action of Ammonia on Diazobenzene. By H. v. PECHMANN and L. FROBENIUS (*Ber.*, 27, 898—900).—The authors conclude that the unstable compound obtained by Griess, by acting on diazobenzene with ammonia, is bisdiazobenzeneamide, since they have obtained bisparadiazotolueneamide from paradiazotoluene in the same way.

Bisparadiazotolueneamide, $NH(N:NC_6H_4)_2$, is obtained by gradually adding a concentrated solution of paradiazotoluene chloride to an excess of ammonia at 0°. It crystallises in lustrous, yellow needles, explodes at 82—83°, or on concussion or by rubbing, and has feebly acid and basic properties. When boiled with acids, it decomposes into nitrogen, cresol, and toluidine. E. C. R.

Diazo- and Isodiazo-compounds. By E. BAMBERGER (*Ber.*, 27, 914—917; see also Schraube and Schmidt; this vol., i, 237, and Bamberger, this vol., i, 295).—Benzenediazoic acid is most easily prepared by adding potassium isodiazo-benzene to an alkaline solution

of potassium ferricyanide, and allowing the mixture to remain about 24 hours.

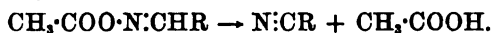
The author has been unable to obtain isodiazocompounds from acetylated nitrosamines. When nitrosoacetanilide is treated with potassium hydroxide, diazobenzene is obtained. This behaviour of acetylated nitrosamines and the fact that they give the colour reactions of diazocompounds when treated with α -naphthylamine is evidence for the existence of the two forms $R \cdot NAc \cdot NO$ and $R \cdot N_2 \cdot OAc$.

E. C. R.

Action of Nitrous Acid on Amidoparadichlorobenzene. By P. HERSCHMANN (*Ber.*, 27, 767—768).—The compounds supposed by Zettel (this vol., i, 22) to be tetrachlorodiazamidobenzene and paradichlorophenylhydrazine have in reality this constitution, for it is possible to convert the latter, by treating it with iodine solution, into dichloriodobenzene; this boils at 250—251°, and yields a mononitroderivative which crystallises in almost colourless needles, and melts at 82°.

C. F. B.

Velocity of Transformation of Aldoximes into Acid Nitriles. By A. HANTZSCH (*Zeit. physikal. Chem.*, 13, 509—530).—The paper contains the results of researches undertaken with the object of determining the effect of various radicles on the rate of decomposition of the acetates of synalldoximes into acid nitriles,



The greatest possible care had to be taken in the preparation of the alldoximes, and especially during the formation of the acetate, a matter frequently of very great difficulty, owing to the extraordinary ease with which many of the compounds were converted into the nitrile during the reaction. The decomposition may be induced by an alkali carbonate, the reaction in this case taking place in two stages, and being therefore of the second order; constant values, however, were not obtainable by the use of sodium carbonate, as it was found that water itself acted as a catalytic agent and effected the decomposition. Water was, therefore, used for the purpose, the compound being dissolved to about N/100 solution in a mixture of 3 vols. alcohol to 2 vols. water, with the addition of a little sodium acetate to prevent etherification of the acetic acid produced. Meta-derivatives as a rule could not be converted into acetate, owing to their ready decomposition. The reaction being of the first order, the velocity constant is given by the equation $C = \frac{1}{t} \log \frac{A}{A-x}$, where $\frac{x}{A}$ is the fraction of the original substance remaining after t minutes. The results are given in the following table (p. 331).

The cyano-derivative gave a decreasing instead of a constant value for C , possibly due to the hydrolysis of the cyanogen group by the acetic acid formed, whilst constant values could not be obtained in the para-nitro-compound, in cinnamic alldoxime, or in para-tolylformoxime. The data are insufficient for a complete elucidation, but variation of the velocity with the chemical nature is plainly indicated, and especially is this so in the case of the halogen compounds.

Metanitrosynbenzaldoxime acetate, $C_6H_5N_2O_4$..	0·000128
Parachlorobenzaldoxime acetate, $C_6H_4(Cl)NO_2$..	0·000371
Thiophensynaldoxime acetate, $C_7H_7SNO_2$	0·000408
Paramethoxybenzaldoxime acetate, $C_{10}H_{11}NO_3$..	0·000410
Piperonalsynaldoxime acetate, $C_{10}H_9NO_4$	0·000474
Paratolylsynaldoxime acetate, $C_{10}H_{11}NO_3$	0·000475
Benzaldoxime acetate, $C_6H_5NO_2$	0·000552
Paraethoxybenzaldoxime acetate, $C_{11}H_{13}NO_3$	0·000564
Parabromobenzsynaldoxime acetate, $C_6H_4BrNO_2$..	0·000619
Paraiodobenzaldoxime acetate, $C_6H_4INO_2$	0·000696
Paracyanobenzaldoxime acetate, $C_6H_5(CN)NO_2$..	0·0008 (P)
Paranitrobenzaldoxime acetate, $C_6H_3N_2O_4$ (at least)	0·0008

Periodobenzaldehyde melts at 77° (not at 73° as stated by Jackson and White); the *antioxime* melts at 122° ; the *synoxime* at 160° , and its acetate at 127° .

Paracyanobenzaldehyde melts at 92° ; the *antioxime* at 180° , the *synoxime* at 143 — 145° , and its acetate at 122 — 124° . L. M. J.

Transformation of Acid-azides into Derivatives of Alkylamines (Substitution of NH_2 for $COOH$). By T. CURTIUS (*Ber.*, 27, 778—781).—Acid-azides when warmed gently in alcoholic solution lose nitrogen and form carbamates (urethanes). For example, benzoylazide, $CPhO\cdot N$, yields the phenylcarbamate $NHPh\cdot COOEt$; nitrobenzoylazide, hippurazide, and fumurazide behave in a similar manner. When boiled with water, benzoylazide yields diphenylcarbamide, $CO(NHPh)_2$, but probably ethylic phenylcarbamate is formed as an unstable intermediate product. With bromine, benzoylazide yields dibromocarbaniol, $NPhBr_2CO$, which loses bromine when heated, forming carbaniol, $NPh\cdot CO$, and this is converted into diphenylcarbamide by water.

To convert an acid, $R\cdot COOH$, into an amine, it is thus necessary to make the ethereal salt, $R\cdot COOEt$, to get the hydrazide, $R\cdot CO\cdot NH\cdot NH$, from this by the action of hydrazine hydrate, to treat it with nitrous acid to form the azide, $R\cdot CO\cdot N_3$, to boil this with alcohol to get the carbamate, $R\cdot NH\cdot COOEt$, or with water to get the carbamide, $(R\cdot NH)_2CO$, and to convert either of these, by heating with strong hydrochloric acid at 120° , into the amine, $R\cdot NH_2$. C. F. B.

Dibromogallanilide and its Triacetyl-derivative. By P. CAZENEUVE (*Compt. rend.*, 118, 540—541).—When finely powdered gallanilide is added to chloroform containing the requisite quantity of bromine, dibromogallanilide is formed with development of heat. It crystallises from dilute methylic alcohol in small, white needles; it is only slightly soluble in boiling water, but crystallises from it with $5H_2O$, which it loses at 100° . Dibromogallanilide does not melt without decomposition; it dissolves in alcohol and in ether. With ferric chloride, its solutions give a blue coloration. When heated with concentrated hydrochloric acid in sealed tubes at 150° , it yields aniline, and a blackish product which probably results from the alteration of

the dibromogallic acid. Bromination, therefore, takes place in the benzene nucleus.

Boiling acetic chloride has no action on dibromogallanilide, but acetic anhydride attacks it somewhat rapidly, yielding a triacetyl-derivative, which crystallises from strong alcohol acidified with acetic acid in small, white crystals, insoluble in benzene or light petroleum, but soluble in chloroform. It does not melt without decomposition, and gives no coloration with ferric chloride. When boiled with alcohol, it yields a di- or monacetyl-derivative, which gives a coloration with ferric chloride.

Attempts to remove the bromine atoms from the nucleus by hydrolysis were unsuccessful. C. H. B.

Benzoic Halogen Amides. By C. E. LINEBARGER (*Amer. Chem. J.*, 16, 216—218).—*Benzoic bromamide*, $\text{COPh}\cdot\text{NHBr}$, was obtained by acting on benzamide with bromine. It crystallises in small plates, melts at 171° , and is soluble in alcohol, alcohol and ether, and benzene. Attempts to substitute the bromine radicle were unsuccessful. Benzoic chloramide was obtained by Bender (*Abstr.*, 1887, 44) by the action of bleaching powder on benzamide. It may also be readily obtained by acting on benzoic bromamide with hydrochloric acid. No corresponding iodo-compound could be obtained. L. T. T.

Action of Phenylisocyanate on Amido-acids. By C. PAAL (*Ber.*, 27, 974—979).—Phenylisocyanate readily combines with the sodium or potassium salts of amido-acids to form phenylureido-derivatives, but with the free acids the reaction is more complex (compare Kühn, *Abstr.*, 1885, 260).

Phenylureidoacetic acid, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$, crystallises from water in long, concentric needles, melts at 195° , and is readily soluble in alkalis and alkali carbonates. The sodium, barium, zinc, and copper salts are crystalline, the last being bluish-green. The ammonium salt readily undergoes dissociation; the aluminium salt is amorphous; the silver salt is stable, and crystallises in colourless, stellate needles; the ethylic salt crystallises in long, thin prisms melting and decomposing at 114° .

α -Phenylureidopropionic acid, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{COOH}$, prepared in a similar manner to the preceding acid, has already been obtained by Kühn.

Orthophenylureidobenzoic acid, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, prepared from sodium orthamidobenzoate and phenylisocyanate, crystallises from dilute alcohol in colourless, needle-like aggregates melting at 181° . The silver salt is stable; the zinc, lead, and copper salts are amorphous. By the action of hydrogen chloride on the acid in alcoholic solution, or by heating the ammonium salt in aqueous solution, 3'-phenyl-2':4'-diketotetrahydroquinazoline, $\text{C}_8\text{H}_6\text{N}_2$ $\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{CO}\cdot\text{NPh} \end{matrix}$

(m. p. 272°), is formed. The yield by the former method is 70 per cent. of the theoretical. *Ethylic orthophenylureidobenzoate* is obtained in small quantity along with the quinazoline; it is readily soluble, and

crystallises in needles melting at 144° . Metaphenylureidobenzoic acid melts at 264° , not 270° as stated by Kühn. J. B. T.

Ureides of Phenylloxamethane. By H. SCHIFF and A. OSTROGOVICH (*Ber.*, 27, 961—963).—Urethanophenylloxamethane,



is prepared by the action of ethylic oxalate on paramidophenylurethane, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{COOEt}$ (this vol., i, 236), and crystallises in acicular plates melting at 131 — 132° . On treatment with alcoholic ammonia, *urethanophenylloxamide*,



is formed, crystallising in colourless needles, and melting and decomposing at 301 — 302° . The *anilide*, $\text{COOEt}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{NHPh}$, forms colourless, flocculent crystals, consisting of microscopic needles, is sparingly soluble, and melts at 351° (corr.). Paramidophenylcarbamide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, and ethylic oxalate yield *uramidophenylloxamethane*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{COOEt}$, crystallising in colourless, slender needles, and melting at 210 — 211° . The *amide*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CONH}_2$, is a colourless, sparingly soluble powder, which does not melt. The substitution of the group NH_2 for OEt in the above urethanes and in similar compounds causes a rise in the melting point of 60 — 80° ; the difference increases with the molecular weight and melting point of the compounds compared.

J. B. T.

Alkylisocarbamides. By F. LENGFELD and J. STIEGLITZ (*Ber.*, 27, 926—927).—When carbodiphenylimide, C(NPh)_2 , is heated at 160 — 190° with anhydrous alcohol, it is converted into *ethylisodiphenylcarbamide* (*ethylic phenylimidophenylcarbamate*),



This substance, which is a colourless oil, resembling glycerol, boils at 200° under a pressure of 20 mm., and is readily soluble in the usual solvents. It combines with hydrogen chloride to form a salt, which decomposes at about 80° , ethylic chloride being evolved and carbaniide left behind. Ethylisodiphenylcarbamide may also be obtained by treating the additive product of carbodiphenylimide and hydrogen chloride with sodium ethoxide. The investigation of these reactions is being continued.

A. H.

Isomerism of Nitrobenzoic acids. By OECHSNER DE CONINCK (*Compt. rend.*, 115, 538—540).—Ortho- and meta-nitrobenzoic acids are much more soluble than the para-derivative in dilute acetic acid, dilute hydrochloric acid, acetone, methylic alcohol, or ethylic alcohol. The para-derivative is only very slightly soluble in methylic and ethylic alcohols. (Compare this vol., i, 289.)

C. H. B.

Separation of Phenylidibromobutyric acid into its Optically Active Constituents. By L. MEYER and O. STEIN (*Ber.*, 27,

890—894).—Inactive phenyldibromobutyric acid is separated into its optically active constituents by crystallising the brucine salts from an alcoholic solution containing 1 mol. brucine to 2 mols. acid, or by employing molecular proportions of the base and acid and fractionally crystallising the salts from alcohol. The dextro-salt is the least soluble. The maximum rotations so far obtained are $[\alpha]_D = +88.3^\circ$ and -54.1° .

E. C. R.

Separation of Cinnamic Dibromide into its Optically Active Modifications. By R. HIRSCH (*Ber.*, 27, 883—888).—Cinnamic acid dibromide cannot be resolved into its optically active modifications by means of inactive bases even if the solution of the salt is sown with crystals of the salt of the optically-active acid. Several optically active alkaloides can, however, be employed for this purpose. The salts of the acid with inactive bases are mostly well crystallised, and the following have been prepared. The *aniline salt*, $\text{PhNH}_2, \text{C}_6\text{H}_5\text{Br}_2\text{O}_2$, crystallises in needles and melts at 112° . The *neutral paratoluidine salt*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2, \text{C}_6\text{H}_5\text{Br}_2\text{O}_2$, forms microscopic crystals and melts at 130° . The *acid paratoluidine salt*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2, 2\text{C}_6\text{H}_5\text{Br}_2\text{O}_2$, melts at 133° . The *quinoline salt* separates in large, transparent crystals, and melts at 118° . The *pyridine salt*, $\text{C}_5\text{NH}_5, 2\text{C}_6\text{H}_5\text{Br}_2\text{O}_2$, crystallises in rhombs and melts at 138° . The *neutral piperidine salt* separates in measurable crystals and melts at 120° with decomposition. The *acid piperidine salt* separates in large measurable crystals and melts at 125° . The *α -naphthylamine salt* forms microscopic crystals and melts at 115° . The *β -naphthylamine salt* melts at 142.5° .

Cinchonine phenyl- $\alpha\beta$ -dibromopropionate is obtained by mixing the base and acid in molecular proportions in absolute alcoholic solution. The precipitated salt yields an acid having the rotation $[\alpha]_D = -16.1^\circ$.

Brucine phenyl- $\alpha\beta$ -dibromopropionate.—When molecular proportions of the base and acid are mixed in a solution of absolute alcohol the precipitated salt yields an acid having the rotation $[\alpha]_D = +13.5^\circ$. If, however, 2 mols. of acid and 1 mol. of base are employed, the salt so obtained yields an acid having the rotation $[\alpha]_D = +21.1^\circ$; and if this salt is fractionally crystallised from absolute alcohol three times, the salt of the dextro-acid is obtained pure and yields an acid having the rotation $[\alpha]_D = +64^\circ$. The salt crystallises in large, measurable crystals and melts at 88° .

Conchinine phenyl- $\alpha\beta$ -dibromopropionate separates in large, colourless crystals and melts at 110° . Only a very partial separation is, however, obtained by this salt, and the acid of highest rotation obtained gave $[\alpha]_D = +9.56^\circ$.

Cinchonidine phenyl- $\alpha\beta$ -dibromopropionate is prepared by mixing molecular proportions of the acid and base dissolved in benzene. The precipitated salt yields an acid having the rotation $[\alpha]_D = -14.4^\circ$. If this salt is extracted with benzene, converted into acid and then again converted into cinchonidine salt and the latter extracted again with benzene, a salt is obtained which yields an acid having the rotation $[\alpha]_D = -63.6^\circ$. The cinchonidine salt crystallises in slender needles and melts at 120° .

E. C. R.

Optically-active Cinnamic Dichloride. By H. FINKENBEINER (*Ber.*, 27, 889—890; compare *Abstr.*, 1893, i, 415).—The author finds that cinnamic acid dichloride is most easily separated into its optically-active constituents by employing the strychnine and acid in molecular proportion, or with a slight excess of the acid. The maximum rotations obtained are $[\alpha]_D = +66.5^\circ$ and -65.9° . No separation can be effected by means of optically inactive bases. Quinine, cinchonine, cinchonidine, narcotine, morphine, and cocaine only afford a very partial separation.

Methylic and ethylic cinnamate dichloride are easily prepared by the usual methods. The methylic salt crystallises well, and melts at $100-101^\circ$; the ethylic salt is a liquid. When prepared from the inactive acid, they are inactive. The salts prepared from the dextro-acid have the rotations, for the methylic salt $[\alpha]_D = +61.9^\circ$, for the ethylic salt $[\alpha]_D = +64.1^\circ$. E. C. R.

Benzophenonoxime from Bisnitrosylbenzhydryl. By W. PLATNER and R. BEHREND (*Annalen*, 278, 359—372).—When diphenylbromomethane is treated with alcoholic or aqueous hydroxylamine, non-nitrogenous products are formed; thus in the latter case benzhydrol ether ($C_{13}H_{11}O$) melting at 108° , is obtained (compare Friedel and Balsohn, *Abstr.*, 1880, 558). *a-Benzyl- β -benzhydrylhydroxylamine*, $CHPh_2 \cdot NH \cdot O \cdot CH_2Ph$, is obtained by warming finely pulverised diphenylbromomethane with benzylhydroxylamine (2 mols.). The *hydrochloride* crystallises in rosettes of white needles, and melts at $193-194.5^\circ$. Attempts failed to effect the removal of the benzyl group by treatment with hydrochloric acid.

When diphenylbromomethane is boiled with acetoxime and acetic acid, *β -benzhydrylhydroxylamine hydrobromide*, $CHPh_2 \cdot NH \cdot OH \cdot HBr$, is obtained; it is purified by conversion into the *oxalate*, which forms small white needles and melts at 171° . The *hydrochloride* melts at 172° . The free base crystallises in small, flat prisms, is readily soluble in water, reduces Fehling's solution, and melts at 78° . *Nitroso- β -benzhydrylhydroxylamine*, $CHPh_2 \cdot N(OH) \cdot NO$, is formed when the hydrochloride of the last-described base is treated with sodium nitrite; it melts at $84-85^\circ$, and does not give Liebermann's reaction. If the nitroso-derivative is dissolved in ether and a few drops of concentrated hydrochloric acid added to the solution *bisnitrosylbenzhydryl*, $N_2O_2 \cdot (CHPh_2)_2$, is obtained together with benzhydrol ether (m. p. 108°). The former crystallises in white needles, melts at $118-120^\circ$, does not give Liebermann's reaction, and is sparingly soluble in all solvents except chloroform. Aqueous alkalis have no action on the compound, but alcoholic alkalis slowly dissolve it, forming benzophenonoxime (m.p. 140°). A. R. L.

Constitution of Triphenylmethane Dyes. By A. ROSENSTIEHL (*J. pr. Chem.*, [2], 49, 317).—With reference to Stock's statement (*J. pr. Chem.*, [2], 47, 403; *Abstr.*, 1893, i, 472) that Hofmann first proposed that these dyes should be regarded as ethereal salts of amido-aromatic alcohols, the author states that he was the first to make this suggestion (*Abstr.*, 1880, 553). A. G. B.

Aurin. By J. HERZIG and T. v. SMOLUCHOWSKI (*Monatsh.*, 15, 73—84; compare Abstr., 1892, 1319).—The acetyl-derivative of aurin, first prepared by Graebe and Caro (Abstr., 1878, 794), is found, when perfectly pure, to melt at 171—172°, and to have the formula $C_{19}H_{13}O_4Ac_3$, and not $C_{19}H_{14}O_3 + Ac_2O$, that previously ascribed to it. The compound must, therefore, be regarded not as a derivative of aurin, but of a substance having the formula $C_{19}H_{14}O_4$. On hydrolysis, however, it is readily converted into aurin, $C_{19}H_{14}O_3$. Acetylaurin is readily reduced to triacetylaurin, and, consequently, contains three acetyl-groups occupying the same position as those in the last-named compound. The authors have not succeeded in recognising the presence of a free hydroxyl-group in acetylaurin.

G. T. M.

Derivatives of Naphthyl Ethyl Ether. By C. DUISBERG (*J. pr. Chem.*, [2], 49, 320).—Heermann (this vol., i, 251) is in error in supposing that the dye-stuffs which he has prepared and referred to in his paper on the above subject, are new; they form the claims in recent patents.

A. G. B.

2 : 3-Naphthylenediamine. By P. FRIEDLÄNDER and S. v. ZAKRZEWSKI (*Ber.*, 27, 761—765).—When 2-naphthol-3 : 3'-disulphonic acid (Abstr., 1889, 515) is fused with caustic soda at 220°, 2 : 3-dihydroxynaphthalene-3'-sulphonic acid is formed, and this, when heated at 180—190° with dilute sulphuric acid, yields 2 : 3-dihydroxynaphthalene, which crystallises in colourless, rhombic plates, melts at 159°, yields no quinone when oxidised, but with 1 mol. of a diazo-compound, and with greater difficulty with 2, gives a dark azo-dye.

2 : 3-Amidonaphthol-3'-sulphonic acid yields dihydroxynaphthalene when heated at 180—200° with dilute acid. If the latter compound is heated with concentrated ammonia at 135—140°, 2 : 3-amidonaphthol is formed; it crystallises in small, brownish needles, melts at 234°, and yields a diacetyl-derivative. If the heating is done at 240°, 2 : 3-naphthylenediamine is formed; this crystallises in greyish plates, melts at 191°, and yields a red azo-dye with 1 mol. of a diazo-compound. Its diacetyl-derivative, $C_{10}H_8(NHAc)_2$, crystallises in brownish needles melting at 247°, and, when boiled with glacial acetic acid, yields an anhydride, $C_{10}H_8 < \begin{smallmatrix} N \\ NH \end{smallmatrix} > CMe$, which crystallises in white needles, and melts at 168°. Moreover, with nitrous acid, 2 : 3-naphthylenediamine yields an azimide, $C_{10}H_8.N_2H$, which crystallises in yellowish needles, melting at 187°; with dihydroxytartaric acid, naphthyl-2 : 3-quinoxalineorthodicarboxylic acid, $C_{12}H_8.N_2(COOH)_2$, is formed in yellow needles melting at 192°, whilst, with oxalic acid, it yields white crystals of dihydroxynaphthylquinoxaline, $C_{12}H_8.N_2(OH)_2$, melting above 350°.

C. F. B.

Chrysene and Chrysofluorene. By C. GRAEBE (*Ber.*, 27, 952—955).—*Isochrysofluorene* (1 : 2- or 1 : 1'-naphthylenephenylenemethane) is prepared by passing the vapour of α -benzyl-naphthalene through a red-hot tube, and is purified by means of the picrate. It is crystalline, and melts at 76°. The presence of chrysofluorene could not be

detected. The *picrate* is yellowish-red, and melts at 122·5°. On oxidation, the hydrocarbon yields a ketone, $\text{CO} < \begin{smallmatrix} \text{C}_{10}\text{H}_8 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, which is red, and has a low melting point. β -Benzyl-naphthalene (free from the α -compound) is converted at high temperatures into chrysfluorene; this melted at 186—187°, and was further identified by oxidation to chrysoketone. The author's previous observation of the formation of β -phenyl-naphthalene, by heating chrysoketone with soda-lime under the ordinary pressure, is confirmed.

J. B. T.

Cycloid Ketoximes. Conversion of Terpene Derivatives into Aliphatic Compounds containing the same Number of Carbon Atoms. By O. WALLACH (*Annalen*, 278, 302—329).—It has been already shown (this vol., i, 46) that cycloid ketoximes undergo isomeric change when treated with phosphorus pentachloride. It is now found that the same change may be readily effected by concentrated sulphuric acid. The nitriles formed by the action of dehydrating agents on cycloid ketoximes (*loc. cit.*) are, without doubt, aliphatic compounds; they appear to be closely related to the odoriferous substances occurring in natural ethereal oils.

When 1-menthonoxime (m. p. 59°) is dropped into concentrated sulphuric acid cooled by ice, it is converted into the isomeride melting at 119—120° (*loc. cit.*). If the latter is dissolved in chloroform and treated with phosphorus pentachloride (1 mol.), hydrogen chloride is evolved, and when the product is mixed with water the oxime is regenerated. When, however, the solvent is distilled off under diminished pressure at a low temperature, a strong bivalent base, $\text{C}_{20}\text{H}_{33}\text{ClN}_2$, is obtained; this crystallises from alcohol in transparent prisms, melts at 59—60°, and probably has the constitution $\text{CH}_3 \cdot \text{CHPr}^s \cdot \text{C} \cdot \text{N} \cdot \text{CH} \cdot \text{CHMe} \cdot \text{CH}_3$, $\text{CHCl} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHPr}^s \cdot \text{C} \cdot \text{NH}$. Its specific rotatory power in alcohol is $[\alpha]_D = -186\cdot35$. Several crystalline salts are described. From the formation of this base, it follows that the isomeride of menthonoxime melting at 119—120°, is not an oxime; probably it has the constitution $\text{CHPr}^s < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}(\text{OH}) \\ \text{C}(\text{NH}) \end{smallmatrix} \cdot \text{CH}_3 > \text{CHMe}$.

In the preparation of the nitrile from menthonoxime and phosphoric anhydride (*loc. cit.*), it is best to use an indifferent diluent; but the nitrile is more readily obtained by treating a chloroform solution of the compound melting at 119—120° (mentioned above) with phosphorus pentachloride; it is also formed when menthonoxime is boiled for a long time. Mentho-nitrile boils at 225—226°, has a sp. gr. at 20° = 0·8355, a specific refractive power $[n]_D = 1\cdot4445$ at 20°; its constitution is probably $\text{CHMe}_2 \cdot \text{CH}(\text{CN}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH}_3$. The *amide*, $\text{C}_8\text{H}_{17} \cdot \text{CONH}_2$, is formed by boiling the nitrile for half an hour with alcoholic soda; it crystallises in satiny plates, and melts at 105—106°. By prolonging the treatment of the nitrile with alcoholic soda, the *acid* $\text{C}_8\text{H}_{17} \cdot \text{COOH}$ is obtained; it forms a sparingly soluble silver salt.

When the nitrile is reduced with sodium and alcohol two bases are

formed which may be separated by means of their oxalates. The first base, *aliphatic menthylamine* (menthonylamine), $C_{10}H_{19}NH_2$, forms a sparingly soluble *oxalate*. The free base boils at $207-208^\circ$, and closely resembles the cycloid menthylamines in odour; its sp. gr. at 20° is 0.8075, and its specific refractive power at 20° is $[n]_D = +1.45$; it is feebly dextrorotatory. Several salts as well as a liquid *acetyl*-derivative and an *oxamide* melting at $82-83^\circ$, were prepared. The second base obtained by the reduction of the nitrile has the formula $C_{10}H_{23}NO$; it boils at $252-253^\circ$.

If menthonylamine nitrite is boiled with water, an alcohol and a hydrocarbon are obtained. The alcohol, $C_{10}H_{19}OH$, is a colourless liquid resembling linalool, and has all the properties of a primary aliphatic alcohol; it boils at $95-105^\circ$ under a pressure of 7 mm., has a sp. gr. at $20^\circ = 0.8315$, a specific refractive power at 20° $[n]_D = 1.44809$, and a specific rotatory power $[\alpha]_D = +2$. The hydrocarbon, $C_{10}H_{18}$, boils at $153-156^\circ$, and has sp. gr. = 1.4345 at 15° . When the last-mentioned alcohol is oxidised with chromic acid, an aldehyde, $C_{10}H_{18}O$, is obtained which is distinguished from the natural products citral, linalool, and geraniol by its intense orange-like odour. A complete comparison of this aldehyde with that from orange-oil has not yet been made. The paper concludes with a lengthy theoretical discussion of these results.

A. R. L.

Isomeric Methylcyanocamphora. By A. HALLER and MINGUIN (*Compt. rend.*, 118, 690-693).—When crude methylcyanocamphor is kept below 0° for some time, crystals are deposited, and can be purified by recrystallisation from a mixture of ether and light petroleum. They are insoluble in water and alkalis, but dissolve in alcohol or ether, melt at 63° , and have a molecular rotatory power $[\alpha]_D = +150.8^\circ$. The crystals have the composition of methylcyanocamphor, and with aqueous hydrochloric acid decompose quantitatively into methylic chloride and cyanocamphor, the latter being soluble in potassium hydroxide. With bromine, the compound yields methylic bromide and a bromocyanocamphor identical with that obtained by the action of bromine on cyanocamphor in presence of carbon bisulphide. Potassium hydroxide in time converts it into hydroxycamphocarboxylic acid, identical with that obtained by the action of the alkali on cyanocamphor, methylic alcohol being, doubtless, formed at the same time.

This modification of methylcyanocamphor, which the authors distinguish as the β -modification, has, in all probability, the constitution $C_8H_{14} \begin{smallmatrix} & C \cdot CN \\ & | \\ C \cdot OMe \end{smallmatrix}$.

The liquid portion has the same composition as the crystals, and can be freed from the last traces of the latter by treatment with hydrochloric acid followed by potassium hydroxide. The purified product, which the authors distinguish as α -methylcyanocamphor, is a thick, yellowish liquid with a rotatory power $[\alpha]_D = +90.1^\circ$. Sometimes it deposits soft, yellow crystals which melt at $38-45^\circ$, and have the same composition and rotatory power as the liquid. Hydrochloric acid has no action on this compound in the cold.

When boiled with alcoholic potash, it yields ammonia and methylhydroxycamphocarboxylic acid, which melts at 175° , and has a rotatory power $[\alpha]_D = +26.31^{\circ}$. It would seem, therefore, that the

α -modification has the constitution $C_8H_{14} < \begin{smallmatrix} CMe \cdot CN \\ CO \end{smallmatrix}$. Schutzen-

berger has supposed that a radicle displacing the hydrogen in cyanocamphor can attach itself either to the $C \cdot CN$ group or the $:CO$ group according to the conditions.

Other alkylid iodides and chlorides act on sodiocyanocamphor, in the same way that methylic iodide does, and it is noteworthy that the higher homologues of methylic iodide yield very small quantities of the α -modifications.

The behaviour of the cyanocamphors affords further evidence that in many compounds the molecular arrangement is unstable and is liable to partial changes in a manner which is not represented by the ordinary constitutional formulæ. C. H. B.

Camphoric acid. By W. A. NOYES (*Ber.*, 27, 917—919).—*Methylic camphoramate*, $NH_2 \cdot CO \cdot C_8H_{14} \cdot COOMe$, is obtained by treating methylic camphorate with phosphorus oxychloride and ammonia. It crystallises in white needles, and melts at 152 — 153° . The *chloride* crystallises in transparent tablets, and melts and decomposes at 244° .

β -*Camphoramie acid* is obtained by heating camphoricimide with 10 per cent. sodium hydroxide solution. It crystallises in lustrous prisms, melts at 182 — 183° , and is different from Claisen and Manasse's acid (*Annalen*, 274, 81).

Dihydroaminocampholytic acid is obtained by heating camphoricimide with aqueous soda, and then warming the mixture with bromine. It crystallises in granules or in nacreous plates, and sublimes without melting. E. C. R.

Tanacetone and its relation to Thujone. By F. W. SEMMLER (*Ber.*, 27, 895—898; compare *Abstr.*, 1893, i, 107).—Tanacetone, $CHPr \cdot CH \cdot CO$

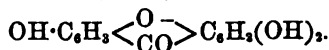
$CH_2 - CH \cdot CHMe$ (b. p. 203°), when heated at 280° for 24 hours in a sealed tube, is converted into a product which boils at 220 — 235° , and, when treated with hydroxylamine, yields an *oxime*, which melts at 92 — 93° . This oxime, when warmed with dilute sulphuric acid, yields pure *carvotanacetone*, $CPr < \begin{smallmatrix} CH \cdot C(OH) \\ CH_2 - CH_2 \end{smallmatrix} > CMe$. This boils at 228° , and has the sp. gr. = 0.9373 at 17° , $[n]_D = 1.4835$. It has an odour closely resembling that of carvone.

Tetrahydrocarvotanacetone, $C_{10}H_{20}O$, obtained by reducing carvotanacetone with sodium and alcohol, boils at 219 — 220° , has a sp. gr. of 0.9014 at 17° , and $[n]_D = 1.4685$. It has an odour resembling that of terpineol, and, in properties, closely resembles hexahydro-oxycymene, obtained by Wallach from terpineol.

Both tanacetone and absinthone, which the author believes are identical, combine with sodium hydrogen sulphite, and yield solid

oximes; whereas thujone and salvone do not, and they also differ from tanacetone in physical properties. E. C. R.

Synthesis of Gentisin. By S. v. KOSTANECKI and J. TAMBOUR (*Monatsh.*, 15, 1—8; compare *Abstr.*, 1891, 1244, and 1386).—When gentisinic acid (hydroquinonecarboxylic acid, $C_6H_3(OH)_2COOH$ and phloroglucinol are mixed in molecular proportion, and, after adding acetic anhydride, the mixture is distilled in small retorts, a small quantity of gentisein, $C_{13}H_8O_6$, is obtained as a sublimate in the neck of the retort; it forms yellow needles. This synthesis, taken in conjunction with previous observations (*loc. cit.*) indicates that gentisein is the 1 : 3 : 7-trihydroxyxanthone,



The methyl ether of gentisein is readily obtained on treating that substance with methylic iodide and potassium hydroxide, and proves to be identical with natural gentisin, $C_{13}H_8O_6 \cdot OMe$.

Dibenzoylgentisin, $C_{14}H_8O_6Bz_2$, whether obtained from the natural or synthetical product, was found to crystallise from alcohol in thick, white needles, and to melt at 192°. The monobenzoyl derivative of gentisin methyl ether, $C_{13}H_8O_6(OMe) \cdot OBz$, crystallises in white, gleaming masses of needles, and melts at 197°. G. T. M.

Isolation of Sugars from Glucosides. By E. SCHUNCK and L. MARSCHLEWSKI (*Annalen*, 278, 349—359).—The authors confirm their previous statement (this vol., i, 142) that the sugar obtained by hydrolysing datiscin is rhamnose. The sugar formed by hydrolysing lupinin (Schulze and Barbieri, *Ber.*, 11, 2220) gives an osazone melting at 204°, identical with ordinary glucosazone. Inasmuch as lupinin sugar is dextro-rotatory and fermentable (*loc. cit.*), the authors consider the proof that it is identical with ordinary glucose to be complete. Rochleder and Schwarz (*Annalen*, 30, 200) consider that æsculin, on hydrolysis, yields a sugar which is not identical with glucose. The authors have prepared the osazone from this sugar; it melts at 205—206°, and in all its other properties is identical with glucosazone. The same remarks apply to the sugars from rubiadin and arbutin; in the latter case, the melting points of the sugar itself (hydrated and anhydrous) are shown to be the same as those of glucose. The authors likewise prove conclusively that the sugar from phloridzin is ordinary glucose. The view recently advanced by Hesse (this vol., i, 104) that the freshly prepared sugar is subsequently converted into glucose perhaps through the agency of micro-organisms, is negated by the fact that the sugar prepared by the authors was kept sterilised, and it was found to be identical with glucose a fortnight after its preparation. The authors have prepared the sugar from crocetin, and converted it into the osazone; this was homogeneous, and had the properties of glucosazone. The sugar from picrocrocetin also gave glucosazone. A. R. L.

Action of Bromine on Datiscetin. By E. SCHUNCK and L. MARSCHLEWSKI (*Annalen*, 278, 346—349).—When datiscetin (this

vol., i, 143) is dissolved in glacial acetic acid and treated with a small quantity of bromine, salicylic acid and bromosalicylic acid are formed; if an excess of bromine is used and the liquid is boiled, bromanil separates on cooling, whilst tribromophenol remains dissolved in the mother liquor. That salicylic acid is the initial product in the latter case is proved by the fact that this acid is readily converted into bromanil and tribromophenol when boiled with bromine in glacial acetic acid solution, and it is incidentally mentioned that this is a convenient and rapid method of preparing bromanil.

A. R. L.

Brasilin and Hæmatoxylin. By J. HERZIG (*Monatsh.*, 15, 139—146; compare Abstr., 1898, i, 426).—The author finds that the amorphous product obtained by the interaction of trimethylbrasilin, acetic anhydride, and sodium acetate gradually becomes crystalline after long exposure to the air. The substance, when deposited from alcoholic solution, forms beautiful, compact crystals, which melt at 172—174° (uncorr.), and, on analysis, prove to be *acetyltrimethylbrasilin*, $C_{18}H_{10}O_8Me_3Ac$. *Tetramethylbrasilin*, $C_{18}H_{10}O_8Me_4$, is readily obtained on heating trimethylbrasilin, potassium hydroxide, and methylic iodide in a water bath for 7—8 hours. It is only sparingly soluble in cold alcohol, from which it crystallises in beautiful, white scales, and melts at 137—138°. Both trimethylbrasilin and tetramethylbrasilin are decomposed by alcoholic potash at 150—160°, yielding products soluble in potash.

On methylation, hæmatoxylin behaves similarly to brasilin. *Tetramethylhæmatoxylin*, $C_{18}H_{10}O_8Me_4$, crystallises from alcohol in slender needles, melts at 139—140°, and, on treatment with acetic anhydride and sodium acetate, gives rise to *acetyltetramethylhæmatoxylin*, $C_{18}H_8O_8Me_4Ac$, which crystallises in beautiful, white needles, and melts at 178—180°. *Pentamethylhæmatoxylin*, $C_{18}H_8O_8Me_5$, is prepared from the tetramethyl derivative by a method corresponding with that used for obtaining tetramethylbrasilin from trimethylbrasilin, and melts at 144—147°.

The observation that all the hydroxyl groups in brasilin and hæmatoxylin do not behave similarly on methylation appears to indicate that in all probability those substances are constituted similarly to xanthone and fluoran.

G. T. M.

Chlorophyll. By E. SCHUNCK and L. MARCHLEWSKI (*Annalen*, 278, 329—345).—According to the authors' experiments, the action of hydrochloric acid on an alcoholic solution of chlorophyll appears to proceed as follows. The chlorophyll is first converted into chlorophyllan (Hoppe-Seyler, *Zeit. physiol. Chem.*, [3], 5; Tschirsch, *Unters. über Chlorophyll*, 1884), and thence into an amorphous substance, phylloxanthin, which is then transformed into fatty acids (?), and a crystalline compound, phyllocyanin. Both phylloxanthin and phyllocyanin form crystalline compounds with copper acetate; that obtained from phyllocyanin gave analytical values indicating the possible empirical formula $C_{58}H_{71}N_3O_{17}Cu_2$. When phyllocyanin is evaporated with hydrochloric acid or treated with alkalis, phylotaonin is obtained.

Hansen believes (*Die Farbstoffe d. Chlorophyll*, 1889) that the treatment of chlorophyll with alkalis consists in the removal of the combined fatty acids by hydrolysis, the colouring matter itself remaining intact. He contends that after such treatment the colouring matter is much purer than before. The authors have observed, however, considerable differences in the absorption spectra of chlorophyll solutions before and after treatment with alkalis, which they consider to be incompatible with Hansen's views (see also below).

When grass is boiled with alcoholic soda, and hydrogen chloride is passed through the filtrate, stellate groups of brown needles having a purple reflex separate, together with sodium chloride. If, after purification, this substance is crystallised from methylic or ethylic alcohol, *methylphyllotaonin* and *ethylphyllotaonin* are obtained respectively. The methyl derivative melts at about 210° ; its greenish-blue solution in concentrated hydrochloric acid exhibits the absorption spectrum observed with phyllocyanin in the same solvent. *Phyllotaonin* is obtained by treating either of the last-described compounds with alcoholic alkali; it has acidic properties. It crystallises from ether in opaque scales having a steel-blue reflex. Analyses of phyllotaonin and of its methyl and ethyl derivatives agree with the formulæ $C_{40}H_{38}N_2O_5 \cdot OH$, $C_{40}H_{38}N_2O_5 \cdot OMe$, and $C_{40}H_{38}N_2O_5 \cdot OEt$ respectively. When phyllotaonin is boiled with glacial acetic acid, an *acetyl* derivative is obtained which gave analytical values in agreement with the formula $C_{40}H_{38}N_2O_5 \cdot OAc$.

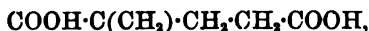
A. R. L.

α -Epichlorhydrin-piperidine Derivatives. By L. NIEMIOWICZ (*Monatsh.*, 15, 118—131).—When piperidine is shaken with an equivalent quantity of α -epichlorhydrin, suspended in 10 times its weight of water, a milky liquid is formed, from which ether extracts a base, characterised by the formation of the following salts. The *hydrochloride* crystallises in prisms, and melts at 156.5° ; the *platinochloride*, $(C_5H_{10}NOCl)_2 \cdot H_2PtCl_6$, crystallises in yellow prisms, which are only sparingly soluble in water. The base is 1-*chlorhydrin-piperidine*, $C_5H_{10}NOCl$, a colourless oil, which decomposes on distillation at ordinary pressures, and on treatment with sodium hydroxide, in anhydrous ethereal solution, gives rise to a new base, *α -epipiperidinehydrin*, $C_5H_{10}NO$. The latter boils without decomposition at 198° (uncorr.), and if left with dilute hydrochloric acid for some time, is converted into 2-*chlorhydrin-piperidine*, which differs from its stereoisomeride, described above, in forming a *platinochloride*, much more soluble in water, and crystallising in golden-yellow scales. Both platinochlorides, however, melt at 189° , with slight decomposition. On evaporating an ethereal solution of 1-chlorhydrin-piperidine, white, cholesterol-like crystals of *piperidiniumhydrin chloride* are obtained. This is insoluble in ether, but dissolves readily in water, yields a characteristic platinochloride, $(C_5H_{10}ONCl) \cdot PtCl_6$, and when gently heated with dilute aqueous sodium hydroxide, is converted into the isomeric *epipiperidinehydrin*. When piperidiniumhydrin chloride is heated, either dry, or in aqueous solution, it forms a vitreous, non-crystalline substance, *piperitiumhydrine chloride*, which yields an amorphous platinochloride, $(C_5H_{10}NOCl) \cdot PtCl_6$. α -Epichlorhydrin and excess of piperidine

give rise to the formation of symmetrical *dipiperidinehydri*n, $C_{13}H_{22}N_2O$, which distils unchanged at 288° (546 mm.), melts at $11-12^\circ$, and forms a platinochloride, $C_{13}H_{22}N_2O, H_2PtCl_6$, crystallising in pyramids or scales. The same base is formed from symmetrical, as well as from unsymmetrical, dichlorhydri

G. T. M.

Decomposition of α -Hydroxynicotinic acid with Nascent Hydrogen. By T. v. SMOLUCHOWSKI (*Monatsh.*, 15, 55—71).—By the action of sodium amalgam on the pyridine-monocarboxylic and -dicarboxylic acids (compare *Abstr.*, 1891, i, 114), the group $—CH:N:CH:$ was resolved eventually into $—CO\cdot O\cdot CH_2—$, and non-nitrogenous acids thereby formed. The author has determined the effect of the reducing agent on a hydroxypyridinecarboxylic acid, namely, α -hydroxynicotinic acid, and finds that in this case the reduction does not occur in so simple a manner, the products varying according to the alkalinity and degree of concentration of the solution. The following substances were isolated in a pure state. *Iso- α -methylglutaconic acid*, $C_6H_6O_4$. This crystallises in monosymmetric prisms, $a : b : c = 0.8360 : 1 : 0.4558$. It is readily soluble in water, melts at 141° , and has the constitution



or more probably $COOH\cdot CMe\cdot CH\cdot CH_2\cdot COOH$. It forms the micro-crystalline salts, $C_6H_6O_4Ba$, and $C_6H_6O_4Ag$, and the dibromide, $C_6H_6O_4Br_2$, which dissolves readily in water, alcohol, and ether, and melts and decomposes at 160° . On further reduction with hydriodic acid, it forms α -methylglutaric acid, which melts at 77° . *Iso- α -methylglutaconamide*, $C_6H_6O_2N + H_2O$, crystallises from water in scales, and melts at $182-183^\circ$ (uncorr.). In addition to these crystalline substances, a syrupy brown liquid was obtained, but this refused to crystallise, even after being kept for several months, and the author has been unable to determine its nature. The formation of iso- α -glutaconic acid in the reaction is in all probability the result of a secondary change, as it is scarcely conceivable that an unsaturated acid could be formed in a solution from which hydrogen was being evolved.

G. T. M.

Halogen Alkyl Derivatives of Isoquinoline. By A. CLAUS (*J. pr. Chem.*, [2], 49, 295—307).—Attention has already been called to the existence in the cinchona alkaloid of a nitrogen atom whose function is similar to that of the nitrogen atom in isoquinoline (*Abstr.*, 1892, 1249). The alkylene bases, also previously described (*Abstr.*, 1892, 1358), must be regarded as having their alkylene groups centrally disposed within the nitrogen ring.

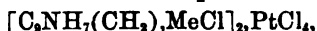
It is shown that the similar derivatives of the cinchona alkaloids probably have an analogous structure, for the decomposition of isoquinoline and of these alkaloids when heated with an alkyl iodide and potassium hydroxide, is of the same deep-seated character, and is attended by the formation of similar products.

Methylene-isoquinoline has been isolated in an impure condition as a

viscid liquid by the action of potassium hydroxide on isoquinoline methiodide; its *methiodide*, $C_9NH_7(CH_2)MeI$, has also been isolated in an impure condition.

Isoquinoline methylidichromate, $C_9NH_7MeCr_2O_7$, is an orange-yellow, crystalline precipitate, thrown down from the aqueous solution of isoquinoline methiodide by potassium dichromate; it decomposes at 218° .

Methylene-isoquinoline methochloride platinochloride,



is a yellow, crystalline, anhydrous powder, and decomposes at 230° .

Bismethyleneisoquinoline is the product of the treatment of methyl-eneisoquinoline methiodide with potassium hydroxide; it is a viscid, insoluble liquid, and readily forms a *methiodide*, which, however, cannot be made the means of introducing another methylene group into the isoquinoline.

A. G. B.

4'-Parahydroxyphenylquinoline. By E. BESTHORN and G. JAEGLÉ (*Ber.*, 27, 907—914).—The authors have prepared 4'-parahydroxyphenylquinoline synthetically from methoxyacetophenone by the method of Claisen and Beyer (*Ber.*, 20, 2178).

Paramethoxybenzoylacetone, $OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot COMe$, is obtained from paramethoxyacetophenone by the action of ethylic acetate and sodium methoxide. It forms beautiful, white crystals, and melts at 54.5° . The *anilide* forms beautiful, bright-yellow crystals, and melts at $111-112^\circ$.

4'-*Paramethoxyphenylquinaldinesulphonic acid* is obtained when the above anilide is treated with concentrated sulphuric acid. It is separated by means of its *barium salt*, $C_{24}H_{28}N_2S_2O_6Ba \cdot 10H_2O$, which crystallises in white needles. The pure acid crystallises in slender, white needles, and when boiled with concentrated hydrobromic acid is converted into 4'-parahydroxyphenylquinaldine hydrobromide. When the above barium salt is heated with benzaldehyde and zinc chloride at 160° , a *benzylidene compound* is obtained.

4'-*Parahydroxyphenylquinaldinic acid*, $OH \cdot C_6H_4 \cdot C_9NH_7 \cdot COOH$, is obtained by oxidising the preceding benzylidene compound with potassium permanganate, and then heating the sulphonic acid so obtained with concentrated hydrobromic acid; it crystallises in yellow needles, melts at $234-235^\circ$ with evolution of carbonic anhydride, and, when heated with acetic anhydride, yields a beautiful, red dye.

4'-Parahydroxyphenylquinoline is obtained by heating the preceding acid at 250° . It melts at 243° , and is identical with the phenolquinoline obtained by Königs and Nef (*Ber.*, 20, 629) from apocinchene.

E. C. B.

5-Methylpyrazole. By R. v. ROTHENBURG (*Ber.*, 27, 955—956).

—Methylpyrazole, $Me \cdot \begin{array}{c} NH \cdot N \\ | \quad | \\ CH \cdot CH \end{array}$, is prepared by the action of hydrazine acetate on sodium acetoacetaldehyde, and has been previously described by G. Marchetti (*Abstr.*, 1893, i, 179). It does not combine with benzaldehyde, and yields no azo-derivative. The

hydrochloride and sulphate are readily soluble. 5-Pyrazolecarboxylic acid, $\text{COOH} \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{smallmatrix}$, is formed by the oxidation of 5-methyl-

pyrazole with potassium permanganate, and is deposited in granular crystals melting at 215—216°. The silver salt decomposes on exposure to light, and, like the acid, yields pyrazole on distillation.

5-Methylpyrazoline, $\text{CHMe} \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH} \end{smallmatrix}$, is prepared by the action of crotonaldehyde on hydrazine hydrate; it is a yellowish oil with a characteristic odour; it boils and partly decomposes at 180°. It yields an oily methylpyrazole on careful oxidation. J. B. T.

The Pyrazole Series. By L. CLAISEN (*Annalen*, 278, 261—273).—Introductory remarks and theoretical considerations on the paper following (next abstract). The fact that 5 : 1-methylphenylpyrazole, obtained from hydroxymethyleneacetone, is identical with that prepared in other ways, seems to furnish evidence that isomeric phenylpyrazoles having one or more diagonal bonds—analogueous to the isindazoles of Fischer and Tafel (*Annalen*, 227, 303)—do not exist.

A. R. L.

Action of Phenylhydrazine on Hydroxymethyleneacetone and on Acetoneoxalic acid. By L. CLAISEN and P. ROOSEN (*Annalen*, 278, 274—296; compare *Abstr.*, 1891, 1106).—The authors have now definitely proved that the product of the action of phenylhydrazine on the sodium compound of hydroxymethyleneacetone (acetoacetaldehyde) is a mixture of 5 : 1-methylphenylpyrazole (2 parts) and 3 : 1-methylphenylpyrazole (1 part). When this mixture is cooled, the latter compound crystallises out; it melts at 37°, and boils at 254—255° under a pressure of 720 mm. (compare Claisen and Stylos, *Abstr.*, 1888, 671; Knorr, *Annalen*, 225, 202; Andreocci, *Atti Acad. Lincei*, 1891, i, 269; ii, 157).

1-Phenylpyrazole-3-carboxylic acid, $\text{NPh} \cdot \text{C} \begin{smallmatrix} \text{N} = \text{C} \cdot \text{COOH} \\ \diagup \quad \diagdown \\ \text{CH} : \text{CH} \end{smallmatrix}$, is obtained by oxidising 3 : 1-methylphenylpyrazole with alkaline permanganate; it crystallises in silky needles, and melts at 146°; the methylic salt melts at 77°.

The compound obtained from phenylhydrazine and ethylic sodacetoneoxalate (acetopyruvate) is 5 : 1-methylphenylpyrazole-3-carboxylic acid, $\text{NPh} \cdot \text{C} \begin{smallmatrix} \text{N} = \text{C} \cdot \text{COOH} \\ \diagup \quad \diagdown \\ \text{CMe} : \text{CH} \end{smallmatrix}$; its properties have been already

described (*loc. cit.*). The phenylazo-derivative, $\text{NPh} \cdot \text{C} \begin{smallmatrix} \text{N} = \text{C} \cdot \text{COOH} \\ \diagup \quad \diagdown \\ \text{CMe} : \text{C} \cdot \text{N} \cdot \text{Ph} \end{smallmatrix}$, prepared by the successive action of diazobenzene chloride and phenylhydrazine on acetoneoxalic acid, crystallises from hot alcohol in yellow, satiny needles, and melts at 206—207° with evolution of gas.

1-Phenyl-3 : 5-dicarboxylic acid (see *loc. cit.*).

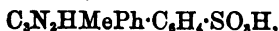
5 : 1-Methylphenylpyrazole was prepared in large quantity by distilling 5 : 1-methylphenylpyrazole-3-carboxylic acid. The authors

find that the pure compound boils at 254—255° (720 mm.), has a sp. gr. at 15° of 1.085, and cannot be solidified when cooled. The platinochloride, when air dried, contains water of crystallisation and melts at 149°; after being heated at 100°, it is rendered anhydrous, and then melts at 171° with decomposition; the methiodide melts at 296° and the ethiodide at 208°. 5 : 1-Phenylpyrazolecarboxylic acid is obtained by oxidising 5 : 1-methylphenylpyrazole with alkaline permanganate; it crystallises in short, white needles and melts at 183°. The *methylic* salt melts at 67°.

3 : 1-Methylphenylpyrazole-5-carboxylic acid is formed in small quantity as a bye-product by the interaction of phenylhydrazine and acetonoallic acid; it crystallises in feathery groups of needles, melts at 189—190°, and, when heated, decomposes into 3 : 1-methylphenylpyrazole; the *methylic* salt melts at 65—66°, and the *amide* melts at 181°.

Dimethyldiphenyldipyrzole, $\text{NPh} \left\langle \begin{array}{c} \text{N}=\text{C}-\text{C}=\text{N} \\ \text{CMe}:\text{CH} \quad \text{CH}:\text{CMe} \end{array} \right\rangle \text{NPh}$, is obtained by the action of phenylhydrazine on a solution of oxalydiacetone in glacial acetic acid; it forms colourless needles, and melts at 142°. The corresponding *tetraphenyl*-derivative, formed by the interaction of phenylhydrazine and oxalydiacetophenone, melts at 232°. A. R. L.

Sulphophenyl- and Hydroxyphenyl-pyrazoles. By L. CLAISEN and P. ROOSEN (*Annalen*, 278, 296—302).—Paraphenyldimethylpyrazolesulphonic acid (Abstr., 1891, 1107) crystallises in rhombic hemimorphic prisms, $a : b : c = 0.5558 : 1 : 0.7889$, containing 1 mol. H_2O . Parahydroxyphenyl-3 : 5-dimethylpyrazole is obtained by fusing the sulphonic acid with potash; it crystallises from hot water in long needles, melting at 166°; the acetyl-derivative melts at 69°. Paraphenylmethylphenylpyrazolesulphonic acid,



is obtained by the interaction of benzoylacetone and phenylhydrazineparasulphonic acid; it crystallises from water in colourless, anhydrous prisms, and yields the *hydroxy*-derivative,

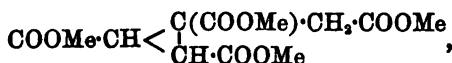


when fused with potash. The latter crystallises in rhombohedra, melts at 206°, and its *acetyl*-derivative at 133°. Paraphenylmethylpyrazolesulphonic acid, $\text{C}_2\text{N}_2\text{H}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, prepared from the sodium-derivative of hydroxymethylenacetone and phenylhydrazine-sulphonic acid, forms yellowish prisms. A. R. L.

Action of Ethereal Diazoacetates on Ethereal Salts of Unsaturated acids. By E. BUCHNER and H. WITTER (*Ber.*, 27, 868—876; see also Abstr., 1893, i, 429).—*Methylic pyrazoline-3 : 4 : 5-tricarboxylate*, $\text{NH} \left\langle \begin{array}{c} \text{CH}(\text{COOMe})-\text{C}(\text{COOMe})-\text{CH}_2\text{COOMe} \\ \text{N}=\text{C}-\text{C}=\text{C}-\text{COOMe} \end{array} \right\rangle$, is obtained by heating methylic aconitate with methylic diazoacetate in

a reflux apparatus at about 60°, and then completing the action by heating in a water bath. It melts at 104°. If, however, the above mixture is heated at once at 100°, then a stereoisomeride is obtained melting at 153°. The compound melting at 104° separates in short, colourless crystals, immediately decolorises permanganate in alkaline solution, gives a white, voluminous precipitate with silver nitrate, and, when hydrolysed with alcoholic potash, yields an acid which sinters at 118°, and melts and decomposes at 155–160°. When treated with hydrogen bromide in cold acetic acid, it is converted into the isomeride melting at 153°; this crystallises in colourless needles, is partially hydrolysed by boiling with water, and immediately decolorises alkaline permanganate solution. It cannot be obtained by treating the isomeride melting at 104° with hydrochloric acid as, under these conditions, hydrolysis takes place, and the acid $C_4H_4N_2(COOMe)_3COOH$ is obtained. This crystallises in colourless needles, melts at 167°, and gives an acid reaction when dissolved in water.

Methylic trimethylene-1 : 2 : 3-tricarboxy-1-acetate,



is obtained by heating the preceding compound at 160–190° under a pressure of 40 mm. mercury as long as nitrogen is evolved. It distils as a colourless oil at 210–215° under 40 mm. pressure. It crystallises in flat prisms and melts at 67°. When boiled with sodium hydroxide solution, it is converted into an “oxyglutaracetic acid,” $C_4H_5(COOH)_3$, which, owing to its extreme solubility, cannot be isolated. When heated with sodium carbonate solution at 60° it yields the lactonic acid, $C_4H_4O_2(COOH)_2$. This crystallises in small, colourless nodules, melts at 190°, is not acted on by alkaline permanganate, and is converted into the preceding oxy-acid when treated with normal solution of sodium hydroxide.

E. C. R.

Action of Ethereal Diazoacetates on Ethereal Salts of Unsaturated Acids. By E. BUCHNER and H. DESSAUVRE (*Ber.*, 27, 877–879; 879–881).—*Methylic methylpyrazoline-3 : 4 : 5-tricarboxylate*, $NH < \begin{array}{c} CH(COOMe) \cdot CMe \cdot COOMe \\ | \\ N = C \cdot COOMe \end{array}$, is obtained by heating methylic

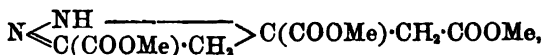
citraconate with methylic diazoacetate at 60°, and gradually raising the temperature to 120°; it crystallises in tufts of long prisms, and melts at 86°. The authors were unable to isolate a stereoisomeride, although, according to theory, this should exist.

Methylic methyltrimethylenetricarboxylate is obtained by decomposing the preceding compound by heat. It distils as a colourless oil at 170–180°, under 30 mm. pressure, crystallises in flat, colourless needles, melts at 77°, and is stable towards alkaline permanganate.

The free acid, $COOH \cdot CMe < \begin{array}{c} CH \cdot COOH \\ | \\ CH \cdot COOH \end{array}$, is obtained by the hydrolysis of the methylic salt. It crystallises in colourless nodules, melts at 191°, without decomposition, and is not acted on by alkaline permanganate.

It is apparently unaltered by boiling with permanganate or with dilute nitric acid.

Methylic pyrazolinedicarboxylate,



is obtained by mixing methylic itaconate and methylic diazoacetate at the ordinary temperature. It crystallises in colourless, interlacing needles, melts at 91°, and is not altered by heating with hydrogen bromide in acetic acid solution. When heated under diminished pressure at 160—180°, it yields a bright yellow oil, which distils at 190—200°, contains no nitrogen, and remains uncrystallised after the lapse of years. This compound quickly decolorises alkaline permanganate, and, when hydrolysed with aqueous sodium hydroxide, yields a mixture of a saturated and an unsaturated acid. The latter, owing to its great solubility, could not be isolated. The saturated acid was identified as a *trimethylene-1:2-dicarboxy-1-acetic acid*. It crystallises in colourless crusts, begins to decompose at 180°, melts at 212° with decomposition, does not decolorise alkaline permanganate, and is not altered by boiling with a normal solution of sodium hydroxide.

E. C. R.

Transformation of Ketazines into Pyrazolines. By T. CURTIUS and H. A. FÖRSTERLING (*Ber.*, 27, 770—773).—If dimethylketazine, $\text{CMe}_3 \cdot \text{N} \cdot \text{N} \cdot \text{CMe}_3$, obtained by the action of hydrazine hydrate on acetone, is treated with maleic acid, or if acetone is treated with hydrazine maleate, *trimethylpyrazoline maleate* is formed. This crystallises in colourless needles, melts at 127°, and is decomposed by dilute acids and alkalis into its constituents; with concentrated caustic soda, however, it yields, not maleic, but fumaric acid. The *trimethylpyrazoline*, $\begin{array}{c} \text{N} = \text{CMe}_3 \\ | \\ \text{NH} \cdot \text{CMe}_3 \end{array} > \text{CH}_2$, obtained from it is identical with that obtained from hydrazine hydrate and mesityl oxide; its *hydrochloride* melts at 170°, its *picrate* at 138°.

Fumaric acid effects the same transformation, but not spontaneously, prolonged heating at 100° being necessary.

Hydrazine maleate, $\text{C}_2\text{H}_2(\text{COOH})_2 \cdot \text{N}_2\text{H}_4 + 2\text{H}_2\text{O}$, forms colourless needles.

C. F. B.

5-Phenylpyrazoline. By R. v. ROTHENBURG (*Ber.*, 27, 788—790).—Cinnamylideneazaine, $\text{N}_2(\text{CH} \cdot \text{CH} \cdot \text{CHPh})_2$, prepared from hydrazine and cinnamaldehyde (Curtius and Jay, *Abstr.*, 1899, 393), when heated at 120° with excess of hydrazine hydrate, yields *5-phenylpyrazoline*, $\begin{array}{c} \text{N} = \text{CH} \\ | \\ \text{NH} \cdot \text{CHPh} \end{array} > \text{CH}_2$, an oil which, when oxidised, does not yield Buchner's 5-phenylpyrazole (*Abstr.*, 1893, i, 282). Buchner's compound is, therefore, probably 3-phenylpyrazole. Hydrochloric acid converts it into a dimolecular polymeride, the platinochloride of which has the formula $2(\text{C}_8\text{H}_9\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6 + 7\text{H}_2\text{O}$.

With hydrazine hydrate, benzoylaldehyde yields what is probably a mixture of 3- and 5-phenylpyrazole. *Sodio-acetoacetaldehyde*

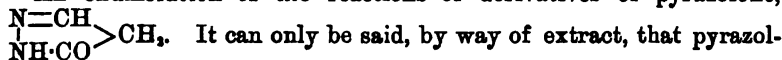
and hydrazine acetate yield methylpyrazole, the platinumchloride of which, $2C_4H_4N_2 \cdot H_2PtCl_6$, was prepared.

Hydrazine hydrate can be prepared, without using a silver retort, by precipitating a boiling solution of hydrazine sulphate with a boiling solution of barium hydroxide, and fractionating the filtered solution. The yield is 70–80 per cent. of the theoretical, and the rest of the hydrazine can be recovered as sulphate from the impure fractions.

C. F. B.

Pyrazolone Reactions. By R. v. ROTHENBURG (*Ber.*, 27, 782).

—An enumeration of the reactions of derivatives of pyrazolone,



It can only be said, by way of extract, that pyrazolones can be readily oxidised, but do not undergo any simple hydrolysis. Substituting and other agents chiefly attack the CH_2 -group, both the hydrogens of which can be replaced by bromine, by the group $:CHR$ from aldehydes, or by $:NOH$ from hydroxylamine, whilst one of them can be replaced by the group $:N.NR$ of diazo-compounds, azo-derivatives being formed. If both these hydrogens are replaced, the product is insoluble in alkalis; if only one, it is soluble, the remaining H doubtless moving to the adjacent C of the CO -group to form the tautomeric pyrazolidone. Nitrous acid forms nitroso-derivatives of pyrazolones, but here the NH -group is doubtless attacked.

C. F. B.

Pyrazolones from Phenylpropionic acid, and their Azo-derivatives. By R. v. ROTHENBURG (*Ber.*, 27, 783–787).—Phenylpropionic acid condenses with hydrazine hydrate to form 3-phenyl-

pyrazolone, $\begin{array}{c} N:CPh \\ | \\ NH-CO \end{array} > CH_2$, melting at 236° . The *benzal* and *isonitroso-derivatives* (compare preceding abstract) melt above 250° and at 184° respectively; the *silver salt* of the latter decomposes at 242° . The *phenyl-, ortho- and para-tolyl-, and α - and β -naphthyl-azo-derivatives* melt at 208° , 179° , 185° , 216° , and above 250° respectively; when reduced, all of them yield, the same *rubazonic acid*, $C_{18}H_{13}N_3O_2$, melting at 124° . With phenylhydrazine, phenylpropionic acid condenses to form Knorr and Klotz's 1:3-diphenylpyrazolone (*Abstr.*, 1887, 1121). The *benzal-* and *isonitroso-*, and the *azo-derivatives* as before, melt at 146° , 199° , 170° , 226° , 242° , 196° , and 225° respectively; on reduction, the *azo-derivatives* all yield the *rubazonic acid*, $C_{20}H_{21}N_3O_2$ (melting at about 200° ?).

3-Carboxypyrazolone-4-orthoazobenzoic acid,



and its *ethylic salt*, melting respectively at 227° and 255° , are obtained from pyrazolone-3-carboxylic acid and its ethylic salt by means of orthodiazobenzoic acid.

The latter part of the paper is devoted to a few remarks on the constitution of pyrazolones, and their relation to isopyrazolones.

C. F. B.

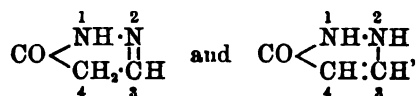
Pyrazolones from Dehydracetic and Coumalinic acids. By R. v. ROTHENBURG (*Ber.*, 27, 790—792).—Dehydracetic acid yields 3-methylpyrazolone when heated at 120° with hydrazine hydrate and a little alcohol. It thus behaves just like ethylic acetoacetate, and this, the author thinks, favours Feist's view as to its constitution.

Dehydrobenzoylacetic acid yields 3-phenylpyrazolone in a similar manner.

Coumalinic acid, under rather different circumstances, yields pyrazolone itself, but it is necessary to work very cautiously, carefully avoiding any violent action. C. F. B.

Isomeric *n*-Phenylpyrazolones. By R. v. ROTHENBURG (*Ber.*, 27, 946—948).—The author maintains, in opposition to Stolz (this vol. i, 259), that the isomeride melting at 118° is 1-phenyl-3-pyrazolone, whilst that melting at 153° has the constitution of a 1-phenyl-5-pyrazolone. A. H.

Nomenclature of the Pyrazolones. By R. v. ROTHENBURG (*Ber.*, 27, 957—958).—Knorr's suggestions, made in 1887 (*Annalen*, 238, 137—219), on this subject are criticised, and the terms *pyrazolone* and *isopyrazolone* are employed to distinguish the groups



instead of 5-pyrazolone and 3-pyrazolone respectively, the positions of substituting elements being indicated by numbers. Knorr's 1-phenyl-3-methyl-5-pyrazolone and 1-phenyl-2 : 3-dimethyl-3-pyrazolone (antipyrine) would therefore be called 1-phenyl-3-methylpyrazolone and 1-phenyl-2 : 3-dimethylisopyrazolone. J. B. T.

New Synthesis of Diketoquinazolines. By A. STEWART (*J. pr. Chem.*, [2], 49, 318).—From the interaction of anthranilic acid, and orthamidobenzamide, respectively, with phenylic isocyanate, compounds are obtained which yield diketo- γ -phenylquinazoline (m. p. 273—274°) when treated with dehydrating agents. The interaction of carbamide with alkylamides directly yields diketo- γ -alkylquinazolines (compare Abstr., 1889, 609); in this way diketo- γ -ethylquinazoline (m. p. 195—196°; Söderbaum, Abstr., 1890, 1254) and diketo- γ -allylquinazoline (m. p. 183°) were obtained. A. G. B.

Formation of Diketoquinazolines from Substituted Anthranilic acids. By W. WIELANDT (*J. pr. Chem.*, [2], 49, 319—320; compare preceding abstract).—By melting benzylanthranilic acid (m. p. 169—170°) with carbamide (equivalent proportions), *carbamido-benzylanthranilic acid*, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{C}_2\text{H}_5) \cdot \text{CONH}_2$, is formed. With excess of carbamide, *benzylidiketoquinazoline*, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \cdot \text{NH} \\ | \quad | \\ \text{N}(\text{C}_2\text{H}_5) \end{array} > \text{CO}$, is produced; it does not melt, but decomposes above 360°. *Phenyl-diketoquinazoline*, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \cdot \text{NH} \\ | \quad | \\ \text{NPh} \end{array} > \text{CO}$, a microcrystalline powder

decomposing above 360° , is the only product of the interaction of phenylanthranilic acid and carbamide.

Trinitrophenylanthranilic acid (m. p. $265-266^{\circ}$) and urea yield *trinitrophenyldiketoquinazoline*, $\begin{matrix} \text{NH}-\text{CO} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{matrix} > \text{N}\cdot\text{C}_6\text{H}_4(\text{NO}_2)_3$, which crystallises in pale yellow needles.

Benzylanthranilic acid and phenylic isocyanate yield the compound $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{C}_6\text{H}_5)\cdot\text{CO}\cdot\text{NHPh}$ (m. p. $165-166^{\circ}$); phenylanthranilic acid and phenylic isocyanate yield *diphenyldiketoquinazoline* (m. p. $234-235^{\circ}$); trinitrophenylanthranilic acid and phenylic isocyanate yield *phenyltrinitrophenyldiketoquinazoline* (m. p. $237-238^{\circ}$); the two latter compounds are also produced by the interaction of the acids with phenylcarbamide.

By substituting thiocarbamide for carbamide, products free from sulphur are obtained. The investigation is proceeding.

A. G. B.

Cinchonifine. By E. JUNGFLISCH and E. LÉGER (*Compt. rend.*, 118, 536—538).—Cinchonifine is best obtained by crystallising from large quantities of strong, boiling alcohol that portion of the cinchonine bases which is insoluble in ether or in dilute alcohol. The cinchonifine separates on cooling, whilst apocinchonine and cinchonidine remain in solution. The purification is accelerated by converting the cinchonifine into basic sulphate, which is crystallised repeatedly from hot water, the free base being subsequently crystallised from boiling alcohol.

Cinchonifine forms small, brilliant, colourless, anhydrous needles, insoluble in water, ether, or dilute alcohol, and very slightly soluble in alcohol or in chloroform, but soluble in a mixture of the two. It melts at 273.6° (corr.) and, when more strongly heated, decomposes and volatilises. It is dextrogyrate in alcoholic solution; at 17° $[\alpha]_D = +201.4^{\circ}$ with a solution of 0.75 gram in 100 c.c., but the rotatory power increases with the concentration. A 1 per cent. solution in dilute hydrochloric acid (2HCl) gives $[\alpha]_D = +228.9^{\circ}$, or with 4HCl + 226.3° ; a 1.5 per cent. solution with 2HCl gives $[\alpha]_D = +225.13^{\circ}$.

Cinchonifine is alkaline to litmus, but not to phenolphthalein; it yields two classes of salts which as a rule are very soluble in water and crystallise well. The basic hydrochloride forms silky needles which contain $2\text{H}_2\text{O}$ and melt at about 208° ; the zincochloride forms anhydrous rhombic prisms; the aurochloride and platinochloride are yellow and imperfectly crystalline; the basic hydrobromide forms very soluble needles which contain H_2O and melt at about 221° ; the basic hydriodide forms colourless, long, flattened prisms which contain H_2O ; the basic nitrate forms highly refractive, rhombic crystals, which contain H_2O ; the basic thiocyanate forms long, flattened anhydrous prisms; the basic sulphate forms efflorescent, prismatic needles, with $2\text{H}_2\text{O}$, but when anhydrous melt at about 188° ; the basic oxalate forms long, slender needles, which contain H_2O , and are much more soluble in hot water than in cold; the basic succinate is very soluble in water, but insoluble in solutions of alkali succinates, and crystallises in prismatic needles,

which contain $1\text{H}_2\text{O}$; the basic tartrate forms flattened elongated prisms which contain $1\frac{1}{2}\text{H}_2\text{O}$ and melt with decomposition at about 209° ; the normal tartrate is less soluble than the basic salt, and crystallises in prismatic needles containing $4\text{H}_2\text{O}$.

Cinchonine methochloride forms large, colourless needles with $2\text{H}_2\text{O}$; the methiodide forms short, anhydrous prisms, which melt with decomposition at 251° , but if crystallised at a low temperature it forms thin plates which contain $2\text{H}_2\text{O}$. The dimethiodide forms very soluble lemon-yellow plates, which contain $1\frac{1}{2}\text{H}_2\text{O}$ and melt and decompose at about 223° . The ethiodide forms long, slender, colourless, anhydrous needles, which melt and decompose at about 251° , and are insoluble in ether; the diiodoethide forms lemon-yellow anhydrous plates which melt with decomposition at about 225° . The ethobromide crystallises with $3\text{H}_2\text{O}$ in bulky prisms which melt and decompose at about 225° , and the diethobromide forms hard, anhydrous, crystalline crusts which melt at about 218° . C. H. B.

Isomeride of Brucine Methiodide. By E. LIPPMANN (*Monatsh.*, 15, 116—117; compare *Abstr.*, 1893, i, 738).—On heating an alcoholic solution of brucine hydriodide with methylic iodide, in sealed tubes, at 100° , a colourless salt is obtained, which is converted by ammonia into an isomeride of brucine methiodide. It crystallises from water in slender prisms, which become transparent at 198 — 200° , and decompose rapidly at 260° . The previously described isomeride, on the other hand, blackens at 270° and decomposes at 280° . The formation of these two isomerides is easily understood, when it is remembered that the two nitrogen atoms in brucine are quite different in their functions, one occurring in a quinoline ring, the other in what is probably either an indole- or a carbazole-group.

G. T. M.

Reducing Substance from Serum-Globulin. By K. A. H. MÖRNER (*Chem. Centr.*, 1894, i, 333—334; from *Centr. Physiol.*, 7, 581—583).—Serum-globulin, precipitated either by the acetic acid or magnesium sulphate method, and heated in the water-bath with 3—5 per cent. hydrochloric acid, yields a substance which reduces Fehling's solution. Serum-globulin coagulated by heat, also that from morbid urine and ascitic fluid, behaves similarly. Myosin, vitellin, crystallin, fibrinogen, serum-albumin, and egg-albumin do not. Fibrin obtained by whipping blood yields a reducing substance, due, probably, to entangled corpuscles. The reducing substance yields an osazone melting at 170 — 172° , is optically inactive, and only feebly reduces alkaline bismuth solutions. W. D. H.

Organic Chemistry.

Nomenclature. By E. SEELIG (*J. pr. Chem.*, [2], 49, 407—408).—The author has elsewhere suggested some changes in the nomenclature of organic compounds; these he indicates in this paper.

A. G. B.

Odour of Alkyllic Sulphides. By J. FINCKH (*Ber.*, 27, 1239—1241).—Commercial amylic sulphide, when heated with powdered copper for 6—8 hours at 290—300°, and subsequently fractionated, had an agreeable, sweet, ethereal smell, but its boiling point and composition were unchanged; the residual copper contained considerable quantities of sulphur, and had a garlic odour. On treating the purified sulphide with a fresh quantity of copper, the latter was practically unchanged. Ethylic sulphide, after being heated three times successively with fresh portions of copper, still retained a trace of its characteristic odour, and methyllic sulphide behaved in the same way; in both cases, small quantities of combustible gas were formed during the experiments, but the boiling point was scarcely affected and the composition remained unaltered. Attempts to deodorise the preceding sulphides by means of olive oil, paraffin, wax, &c., were unsuccessful. Ethyl mercaptan resembles ethylic sulphide in its behaviour towards copper, but a considerable quantity is decomposed during the process.

J. B. T.

Polyhydric Alcohols Synthesised from Aldehydes and Ketones by Means of Formaldehyde. By M. APEL and B. TOLLENS (*Ber.*, 27, 1087—1090).—Tollens and others (*Abstr.*, 1892, 127; 1893, 617) have shown that formaldehyde reacts with other aliphatic aldehydes, yielding polyhydric alcohols; several CH_2OH groups derived from the formaldehyde replace hydrogen atoms in the hydrocarbon residue of the second aldehyde.

Pentaglycol, $\text{CMe}_2(\text{CH}_2\text{OH})_5$, is obtained on warming a mixture of isobutylaldehyde, formaldehyde, calcium hydroxide, and water, removing the calcium by means of oxalic acid, and distilling the solution after evaporation. It melts at 129° and boils at about 110° in a vacuum. The *diacetyl* derivative is a liquid boiling at about 85° in a vacuum, whilst the *dibenzoyl* derivative forms crystals melting at 53°.

Mayer (*Annalen*, 265, 340) found that a mixture of formaldehyde, acetone, calcium hydroxide, and water, yielded a viscid liquid after removal of the lime; the authors have obtained this product in a crystalline state. It is the *anhydride*, $\text{C}_6\text{H}_{12}\text{O}_8$, of the heptahydric alcohol, $\text{OH}\cdot\text{CH}(\text{C}[\text{CH}_2\text{OH}]_2)_2$, and is, consequently, itself a pentahydric alcohol; it melts at 156°. The *pentacetyl* derivative, $\text{C}_6\text{H}_{12}\text{O}(\text{OAc})_5$, melts at 84°, and the *tetrabenzoyl* derivative at 153—154°.

W. J. P.

Combination of Iodine with Starch. By E. G. ROUVIER (*Compt. rend.*, 118, 743—744).—When an aqueous solution of starch is mixed with iodine in excess, but in quantity insufficient to form the com-

pound ($C_6H_{10}O_5$)_nI_n, the quantity of iodine absorbed increases with the quantity added (Abstr., i, 1893, 683). The proportion of iodine that enters into combination for a given quantity of iodine added decreases, however, as the percentage of iodine in the product increases. When this percentage is between 13 and 17.5, the quantity of iodine taken up is practically equal to the cube root of the quantity of iodine added. Below 13 per cent., the quantity of iodine taken up increases more rapidly, but, on the other hand, above 17.5 per cent. it increases much more slowly.

Rice starch behaves in exactly the same way as wheat starch, but potato starch seems to combine with a smaller proportion of iodine even in presence of a large excess of the latter. C. H. B.

Natural Oxycelluloses. By C. F. CROSS, E. J. BEVAN, and C. BEADLE (*Ber.*, 27, 1061—1065 and 1456).—The authors have previously shown (this vol., i, 63) that the production of furfuraldehyde by distilling celluloses with a mixture of sulphuric and hydrochloric acids is not conditioned by the presence of a pentaglucose group in the molecule. They now characterise more fully a group of oxycelluloses containing more oxygen and less carbon than normal cotton-wool celluloses; these yield furfuraldehyde on heating with sulphuric and hydrochloric acids, but give none of the reactions of the pentoses or pentosans; they are, moreover, characterised by their relative stability in respect of alkaline hydrolysis.

The celluloses of the grasses were first examined; of these, the oat-straw and esparto celluloses were found to yield well-characterised oxycelluloses of the above type. These celluloses contain 41—42 per cent. of carbon and 5.4—5.8 per cent. of hydrogen, and on distillation with the mixed acids give 12—12.5 per cent. of furfuraldehyde. Such "celluloses" as these must be distinguished from the normal ones, and may be classified as oxycelluloses. They are further characterised by giving a yellow colour with salts of phenylhydrazine, which becomes more intense on heating; they also give a magenta colour with magenta decolorised by sulphurous acid, and reduce boiling Fehling's solution.

The authors are continuing the investigation; more especially in its bearings on plant physiology. W. J. P.

Oxidation of Unsaturated Brominated Hydrocarbons. By C. H. v. HOESSLE (*J. pr. Chem.*, [2], 49, 403—406).—The oxidation of brominated unsaturated hydrocarbons by alkaline permanganate produces hydroxyketones or hydroxyaldehydes, as expressed by the general equation $R^1CBr:CHR^2 + O + H_2O = R^1CO \cdot CH(OH)R^2 + HBr$.

Vinyllic bromide yields glycolaldehyde; β -bromopropylene yields acetol; bromopseudobutylene yields methylacetylcarbinol (dimethylketol); bromobutylene yields α -hydroxybutyric aldehyde, and bromocinnamene yields the aldehyde $OH \cdot CHPh \cdot CHO$ by such oxidation. Bromostilbene and bromophenanthrene are not attacked.

A. G. B.

Butylchloral. By M. TARUGI (*Gazzetta*, 24, i, 229—236).—The author confirms Pinner's description (*Annalen*, 179, 40), of α - and

β -butylchloralacetamide; they melt at 158° and 170° respectively. The α - and β -butylchloralbenzamides, however, melt at 135° and 146° respectively, instead of at 150° and 170° as stated by Pinner.

Two *butylchloralformamides*, $C_4H_9MeCl_2 \cdot CH(OH) \cdot NH \cdot COH$, are produced by the interaction of formamide and butylchloral; they may be separated by crystallisation from dilute alcohol. The α -compound melts at 125° and the β - at 132° .

On distilling α - and β -butylchloralacetamides with dilute sulphuric acid, they seem to yield the same butylchloral hydrate. The two hydrates are, however, certainly different, for on treating the one derived from the α -amide with acetamide the α -compound is regenerated, whereas the hydrate from the β -amide yields β -butylchloralacetamide (compare Schiff, Abstr., 1891, 1067). The difference does not seem to be due to optical isomerism.

W. J. P.

Amidoketones of the Fatty Series. By S. GABRIEL and T. POSNER (*Ber.*, 27, 1037—1045).—Amidopropyl methyl ketone, $COMe \cdot CHEt \cdot NH_2$ (Abstr., 1893, i, 734), is partially converted into dimethyldiethylpyrazine when its hydrochloride is treated with soda.

Benzenesulphamidopropyl methyl ketone, $SO_2Ph \cdot NH \cdot CHEt \cdot COMe$, obtained by the action of benzenesulphonic chloride on the hydrochloride of the base, forms a white crystalline powder melting at 121° . Potassium cyanate reacts with the hydrochloride of the base

to form ethylmethylimidazolone, $CO \begin{smallmatrix} \text{NH} \cdot \text{CMe} \\ \parallel \\ \text{N} - \text{CEt} \end{smallmatrix}$, which crystallises

from hot water in colourless plates melting and decomposing at 270° . Potassium thiocyanate reacts in a similar manner, forming *ethyl-*

methylimidazolyl- μ -mercaptan, $SH \cdot C \begin{smallmatrix} \text{NH} \cdot \text{CMe} \\ \parallel \\ \text{N} - \text{CEt} \end{smallmatrix}$, which crystallises in

yellowish plates, is soluble in alkalis, and does not melt below 320° . Oxidation by means of alcoholic ethylic nitrite converts the base into

ethylmethylglyoxaline, $HC \begin{smallmatrix} \text{NH} \cdot \text{CMe} \\ \parallel \\ \text{N} - \text{CEt} \end{smallmatrix}$, the *picrate* of which melts at

155 — 158° , and the *aurochloride* at about 167° . It is uncertain whether these compounds are $\alpha\beta$ - or $\beta\alpha$ -derivatives. Investigations are in progress to ascertain whether the base employed in these experiments is identical or isomeric with that obtained by the reduction of the isonitrosoketone described by Claisen and Manasse (Abstr., 1889, 584) as having the constitution $COPr \cdot CH \cdot NOH$.

Derivatives of Amidoacetone.—The compound formed by the action of potassium thiocyanate on amidoacetone hydrochloride, is completely decomposed by nitric acid at 220° , and is also oxidised by bromine water, carbamide being formed. A mercaptole could not be prepared directly from amidoacetone, but *phthalimidoacetone ethylmercaptole*, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CMe(SEt)_2$, is formed when acetonylphthalimide is treated with ethylic mercaptan. It crystallises in colourless tablets melting at 71 — 72° , and is decomposed by hydrochloric acid with formation of phthalic acid, ethylic mercaptan, and amidoacetone.

Derivatives of Diamidoacetone.—Diamidoacetone, first obtained by Rügheimer (Abstr., 1889, 249), may also be obtained in small

amount, by the oxidation of hydroxytrimethylenediphthalimide (Abstr., 1888, 1294), by means of chromic acid. The *diphthalimidoacetone*, $\text{CO}(\text{CH}_2\cdot\text{N}:\text{C}_6\text{H}_4\text{O}_2)_2$, thus formed, is only slightly soluble in the usual solvents, melts at $264\text{--}268^\circ$, and forms pointed crystals. The corresponding *amic acid*, $\text{CO}(\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH})_2$, is a white, crystalline powder, melting at $105\text{--}107^\circ$. The amic acid is decomposed by strong hydrochloric acid, impure diamidoacetone being formed.

Derivatives of Diacetoneamine.—Diacetonedithiocarbamic acid,



is prepared by the action of carbon bisulphide on diacetoneamine in benzene solution. It forms colourless crystals, and melts at $119\text{--}120^\circ$. *Diacetonethiocarbimide*, $\text{C}_6\text{H}_{11}\text{O}\cdot\text{NCS}$, is prepared in the usual way from the foregoing compound. It is a colourless oil which decomposes when distilled. On treatment with an aqueous solution of hydrazine, it is converted into *diacetoneethiosemicarbazide*,



which is soluble in hot water, forms rhombohedral crystals, and melts at $148\text{--}151^\circ$. On treatment with sulphuric acid, it is converted into an *anhydro-compound*, $\text{C}_7\text{H}_{13}\text{N}_2\text{S}$, which forms a crystalline powder melting at $211\text{--}214^\circ$.
A. H.

Preparation of Blue Copper Acetate. By C. ASTRE (*Chem. Centr.*, 1894, i, 141; from *J. Pharm.* [5], 28, 542).—Wöhler states that these blue crystals are easily obtained by crystallising a solution of verdigris acidified with acetic acid. The author finds, however, that they are only formed when the density of the solution at 15° is 1.150 or above. In solutions of slightly lower density, a mixture of blue and green crystals is formed, and in those of less than 1.10, only green crystals. The blue crystals also form when moist verdigris is exposed to low temperatures.
L. T. T.

β -Dimethylacrylic acid. By W. MASSOT (*Ber.*, 27, 1225—1228).—When acetone is heated with malonic acid in the presence of acetic anhydride, dimethylacrylic acid, or isopropylideneacetic acid, $\text{CMe}_2\text{CH}\cdot\text{COOH}$, is formed, although the reaction does not occur when acetic acid is used instead of the anhydride (Komnenos, *Annalen*, 218, 168). The acid crystallises from hot water in long, white needles melting at 69° . It combines with 1 mol. of bromine to form $\alpha\beta$ -dibromisovaleric acid which is decomposed by the action of aqueous alkalis, α -bromisobutylene being formed. This substance is accompanied by a certain amount of α -bromo- β -dimethylacrylic acid, $\text{CMe}_2\text{CBr}\cdot\text{COOH}$, which crystallises in colourless needles melting at $87.5\text{--}88.5^\circ$.

It has been found very difficult to prepare the corresponding chlorine derivatives of dimethylacrylic acid in a state of purity. *Monochlorodimethylacrylic acid* melts at $80\text{--}81^\circ$.
A. H.

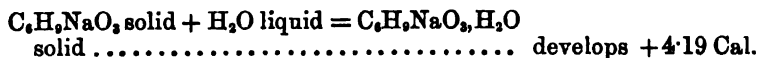
Ethyl Sodacetoacetate. By DE FORCAND (*Compt. rend.*, 118, 922—925).—With the object of throwing further light on the con-

stitution of ethylic sodacetate by determining its thermochemical constants, the author has first prepared the sodium derivative, starting from the pure ethereal salt boiling at $179.5-180.5^{\circ}$ under 760 mm.; sp. gr. = 1.027 at 15° . The direct action of the metal on excess of the salt results in the formation of compounds containing excess of the ethereal salt, which cannot be expelled by heat, because the sodium derivative decomposes below 100° . Elion's process of acting on a solution of the ethereal salt in ether with dry sodium hydroxide suspended in ether, and Gevekoht's method of dissolving the calculated quantity of sodium in an ethereal solution of the salt, give products containing too high a proportion of sodium. Harrow's method of dissolving sodium in ethyl alcohol, adding ether, mixing with the calculated quantity of ethylic acetate dissolved in ether, and then adding water (*Annalen*, 201, 141), yields a pure hydrated salt, which, when dried on porous tiles, contains 13.33 per cent. of sodium, whilst the salt $C_6H_5NaO_2, H_2O$ would contain 13.53 per cent. More water is necessary to cause precipitation of the salt than is indicated by Harrow. When placed in a vacuum over phosphoric anhydride, the salt gradually loses water, without forming any definite hydrates intermediate between the monohydrate and the anhydrous salt.

The following results were obtained for the heat of dissolution at $+12^{\circ}$.

$C_6H_5NaO_2, H_2O$	+0.20 Cal.
$C_6H_5NaO_2, \frac{11}{5}H_2O$	+1.76 „
$C_6H_5NaO_2, \frac{1}{2}H_2O$	+2.38 „

Comparison of these numbers shows that the heat developed is practically proportional to the fraction of a molecule of water added or lost. It would follow that



The partially dehydrated salt when dissolved in water and heated with dilute sulphuric acid gives the same development of heat as the hydrated salt, and hence the loss of water involves no change of constitution.

The author adopts $+4.19$ Cal. as the heat of hydration of anhydrous ethylic sodacetate, and $+4.39$ for its heat of dissolution in 4 litres of water at $+12^{\circ}$. C. H. B.

Reduction of Ethylic Isonitrosoacetate. By S. GABRIEL and T. POSNER (*Ber.*, 27, 1141—1144).—Ethylic isonitrosoacetate is reduced by tin and hydrochloric acid to *ethylic α -amidoacetate*, $CM_2O \cdot CH(NH_2) \cdot COOEt$, the *hydrochloride* of which melts at 95° (it was mixed with a little ammonium chloride), the *picrate* at 129° . This substance in alkaline solution oxidises in the presence of air, to Wleügel's ethyl ketinedicarboxylate (dimethylpyrazinedicarboxylate), $C_4N_2Me_2(COOEt)_2$ (*Abstr.*, 1882, 949); if it is mixed with aqueous potash and some copper sulphate, and distilled with steam, dimethylpyrazine is formed. When the hydrochloride is heated at 60° with phenylhydrazine, acetic acid, and aqueous sodium acetate,

Knorr's phenylmethylpyrazoloneazobenzene, $\begin{matrix} \text{N}=\text{CMe} \\ \text{NPh}\cdot\text{CO} \end{matrix} > \text{C:N}\cdot\text{NHPh}$ (Abstr., 1887, 602), is formed. When heated with potassium thiocyanate on the water-bath, it yields *ethylic mercaptomethylimidazole-carboxylate*, $\begin{matrix} \text{CMe}\cdot\text{N} \\ \text{COOEt}\cdot\text{C}-\text{NH} \end{matrix} > \text{C}\cdot\text{SH}$, melting, with decomposition, at 229° . Heated with potassium cyanate, it yields *ethylic methylimidazolonecarboxylate*, $\begin{matrix} \text{CMe}\cdot\text{NH} \\ \text{COOEt}\cdot\text{C}-\text{NH} \end{matrix} > \text{CO}$, melting at $220-221^\circ$.

C. F. B.

Action of Hydroxylamine and Ethoxylamine on Ethylic Oxalate. By W. LOSSEN (*Ber.*, 27, 1105—1114).—When, to a solution of hydroxylamine hydrochloride (2 mols.) in the equivalent amount of baryta water, ethylic oxalate (1 mol.) is added, and caused to dissolve by shaking, a salt of an isomeric, bibasic, oxalhydroxamic acid, $\text{C}_2\text{H}_4\text{N}_2\text{O}_4$, is formed. The *barium*, *hydrogen*, *silver*, *calcium* ($4\text{H}_2\text{O}$), and *copper* (H_2O) salts of this acid were prepared; they all explode violently when heated to 50° , and mineral acids decompose them entirely, with formation of oxalic acid.

When ethylic oxalate (1 mol.) is gradually added to a methyl alcoholic solution of free hydroxylamine (3 mols.), the hydroxylamine salt of the ordinary oxalhydroxamic acid separates. This is the best method of preparing the acid.

When, to a solution of hydroxylamine hydrochloride (2 mols.) in the equivalent amount of alcoholic potash, ethylic oxalate (1 mol.) is added (after filtering from the precipitated potassium chloride), monobasic *hydroxyloxamic acid*, $\text{COOH}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$ (perhaps, rather, *oxalmonhydroxamic acid*, $\text{COOH}\cdot\text{C}(\text{NOH})\cdot\text{OH}$), is formed. The *sodium* and *potassium* salts were prepared; they are very explosive. The *ethylic* salt was obtained, mixed with some of the acid, by mixing absolute alcoholic solutions of hydroxylamine and ethylic oxalate; by mixing methyl alcoholic solutions of hydroxylamine and methylic oxalate, the *methylic* salt, melting at 120° , was obtained. When the ethylic salt is decomposed with alcoholic potash, the *derivative*, $\text{C}_2\text{HNO}_4\text{K}_2 + \frac{1}{2}\text{H}_2\text{O}$, is formed, from which a corresponding *lead derivative* was prepared; the acid here functions as bibasic. Further, the methylic salt behaves like a monobasic acid; the methyl group is not displaced by the action of potash or ammonia, but the derivatives $\text{C}_2\text{HMeNO}_4\text{Na} + \text{C}_2\text{H}_2\text{MeNO}_4$, and $\text{C}_2\text{H}_4\text{NO}_4(\text{NH}_4)$ are formed. The latter is, doubtless, identical with Hantzsch's ammonium oxaminehydroxamate (this vol., i, 274). Hydroxylamine converts the methylic salt into a hydroxylamine salt.

When ethoxylamine (2 mols.) is mixed with ethylic oxalate (1 mol.) *ethylic oxalhydroxamate*, $\text{C}_2\text{H}_2\text{N}_2\text{O}_4\text{Et}$, melting at 153° , is formed. This functions as a bibasic acid; the very hygroscopic *potassium derivative*, and the *sodium*, *zinc*, *copper*, and *silver derivatives* were prepared; the *dimethylic derivative* was obtained as a colourless oil.

Ethylic iodide yields with silver oxalhydroxamate the compound

$C_2N_2O_4Et_4$; methylic iodide the corresponding compound, $C_2N_2O_4Me_4$; both are transparent oils.
C. F. B.

Elimination of Carbonic Anhydride from Alkyl Substituted Malonic acids. By E. HJELT (*Ber.*, 27, 1177—1178).—The author has previously shown the influence of substituting groups on the relative speed of formation of anhydrides and lactones in this series of acids (*Abstr.*, 1893, i, 693). The following determinations were made by heating 0.5 gram of each acid for 20 minutes at 145° , and titrating the residue with baryta water; the percentages of acid decomposed were as follows:—Malonic acid, 42.9; methylmalonic acid, 39.2; ethylmalonic acid, 42.5; propylmalonic acid, 44.9; isopropylmalonic acid, 37.4; allylmalonic acid, 63.4; benzylmalonic acid, 69.8. The behaviour of the last two acids is due to the negative nature of the radicles; the influence of the isopropyl group is remarkable, as its presence greatly accelerates the formation of anhydrides. This reaction is conditioned chiefly by the chemical nature of the substituting radicles, and the influence which they consequently exercise on the stability of the atomic linkage; their weight and size appear to be of secondary importance.
J. B. T.

Bromo- and Hydroxy-derivatives of Sebacic acid. By M. WEGER (*Ber.*, 27, 1210—1218).—When sebacic acid is treated with bromine and phosphorus tribromide, it is converted into a mixture of bromo-derivatives, from which white crystals melting at about 117° , and corresponding in composition with dibromosebacic acid, can readily be isolated by fractional precipitation from solution in aqueous sodium hydrogen carbonate, or by extraction of the crude mass with cold benzene. This acid has already been obtained (Claus and Steinkauler, *Abstr.*, 1888, 133; Auwers and Bernhardt, *Abstr.*, 1891, 1191), and is described as melting at about the temperature mentioned above. When, however, the crude mass is fractionally precipitated from ethereal solution by light petroleum, and the highest melting portions, thus isolated, further purified by conversion into the calcium salt, an acid is finally obtained, which melts sharply at 136° , and is the pure dibromosebacic acid. It is extremely soluble in alcohol, &c., slightly soluble in cold benzene, almost insoluble in light petroleum.

It was found impossible to isolate any definite substance containing less bromine from the oily portions of the brominated product.

Tetrabromosebacic acid, $C_{10}H_{14}Br_4O_4$, is formed when sebacic acid is heated with a large excess of bromine. It crystallises in plates, melts and decomposes at 165° , and is very readily soluble in ether, readily in benzene, and almost insoluble in light petroleum. The sodium salt, $C_{10}H_{12}Br_4O_4Na_2 + 9H_2O$, effloresces in the air.

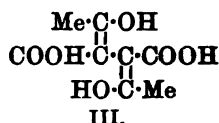
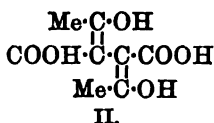
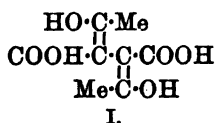
When a solution of the normal sodium salt of the pure acid is boiled, dihydroxysebacic acid is produced. It forms efflorescent crusts, melts at 124° , and is readily soluble in cold water. On oxidation, it is converted into adipic and oxalic acids.

Monhydroxysebacic acid may be prepared from the sodium salt of the oily portion of the product of bromination of sebacic acid. It is

almost insoluble in cold water, and melts at 116°. On oxidation, it is converted into suberic and oxalic acids.

The acids described by Claus and Steinkauler (*loc. cit.*) were prepared from the impure bromo-product, and were themselves probably impure. A. H.

Constitution of Ethylic Diacetosuccinate. By L. KNORE and F. HABER (*Ber.*, 27, 1151—1167).—The isomeric relationships of the α -substituted ethylic acetates, of which ethylic diacetosuccinate is one, are first considered with the consequences resulting from their being (1) ketonic acids, (2) unsaturated alcoholic acids, (3) both ketonic and alcoholic acids in terms of Laar's hypothesis. In the first case, ethylic diacetosuccinate would exhibit the same isomeric forms as the tartarates. In the second case, it must exist in three stereo-isomeric forms,



I would not yield either a γ -lactone or a furfuraldehyde derivative;

II would yield a lactone of the formula $\text{COOH}\cdot\text{C}\cdot\text{C}\cdot\text{CO}$; III would

yield a dilactone, $\text{CO}\cdot\text{C}\cdot\text{C}\cdot\text{CO}$, and also dimethylfurfurandicarboxylic

acid, $\text{COOH}\cdot\text{C}\cdot\text{C}(\text{COOH})\cdot\text{CMe}$. If ethylic diacetosuccinate is a tautomeric compound, six forms would be possible, and these are fully discussed and illustrated in the original paper.

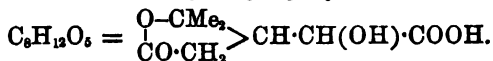
Details of the preparation of ethylic diacetosuccinate by the action of iodine on ethylic sodacetoacetate are given; the yield is 40 per cent. of the theoretical. No isomeric compound is formed, and attempts to resolve it into active components by the action of *Penicillium glaucum*, *Potritis cynerea*, and *Saccharomyces ellipsoideus*, were unsuccessful. On heating the ethylic salt, alcohol is eliminated, and ethylic isocarbotritartrate (ethylic diacetosuccinate γ -lactone) is formed, together with varying quantities of ethylic and diethylic dimethylfurfurandicarboxylates. Ethylic isocarbotritartrate is also formed by the action of alcoholic potash on ethylic diacetosuccinate, and the latter compound is regenerated from the former by heating with alcohol at 180°. It melts at 110°, and cryoscopic molecular weight determinations agree with the formula $\text{C}_{10}\text{H}_{11}\text{O}_5$. The dibromo-derivative, $\text{C}_{10}\text{H}_9\text{Br}_2\text{O}_5$, is insoluble in water, and crystallises in lustrous plates melting at 122°. The nitro-derivative, $\text{C}_{10}\text{H}_9\text{O}_5\cdot\text{NO}_2$, is crystalline, melts at 58—59°, and dissolves in alkalis with a yellowish-red colour. The corresponding compound of ethylic diacetosuccinate, $\text{C}_8\text{H}_{11}\text{O}_5\cdot\text{NO}_2$, crystallises from alcohol in colourless plates, melts at

55°, is insoluble in alkalis, and does not give Liebermann's reaction. By the action of ammonium acetate on ethylic isocarbopyrotartarate, a compound $C_{10}H_{12}NO_4$, is formed, which crystallises from alcohol, melts at 220—221°, and does not show the pyrroline reaction. With aqueous ammonia, the ethereal salt yields a substance which crystallises from water, melts at 260°, and evolves ammonia on heating with soda. Unsymmetrical diphenylhydrazine yields a compound which crystallises in needles, melts at 187°, is not acted on by alkalis and hydrochloric acid, but dissolves in concentrated sulphuric acid; on adding nitric acid, a blue coloration is produced, changing to green and dull yellow.

By the action of alkalis on the lactone, crystalline salts of diacetosuccinic acid are formed; the *free acid* is unstable, and could not be isolated, like the alkali salts, it is converted into acetylacetone on boiling in aqueous solution. This hypothetical acid differs considerably from the diacetosuccinic acid previously prepared by the hydrolysis of ethylic diacetosuccinate with concentrated soda (*Ber.*, 20, 171), the latter is therefore termed the α -form, and the unstable one the β -modification. Attempts to prepare a dilactone from the lactone were unsuccessful; on heating with concentrated sulphuric acid, it is converted into carbopyrotartaric acid. The *strychnine salt* of the lactone crystallises in needles, and melts at 227—228°; failure to obtain an active acid from it renders the ketone formula for the lactone unlikely. The lactone and its ethereal salt spontaneously decompose, more or less rapidly, with formation of acetic acid.

These results indicate that β -diacetosuccinic acid has the formula II (see above), as this explains the ease with which it forms a monolactone, and the non-production of a dilactone. α -Diacetosuccinic acid is therefore either structurally isomeric with the β -acid, $COOH \cdot CHAc \cdot CHAc \cdot COOH$, or it has the formula I; in the former case, their relationship would be similar to that of the two forms of tribenzoylmethane, dibenzoylacetone, and ethylic formylphenylacetate. The formation of carbopyrotartaric acid from α -diacetosuccinic acid and from isocarbopyrotartaric acid is preceded by the conversion of both α - and β -diacetosuccinic acids into the γ -configuration, formula III (see p. 360). J. B. T.

Hydroxyterpenylic acid. By O. BEST (*Ber.*, 27, 1218—1225). —When carvole is treated with aqueous potassium permanganate, it is converted into acetic acid, a non-volatile syrupy acid, which has not yet been examined, and *hydroxyterpenylic acid*,



The latter crystallises from hot water in colourless needles, and melts at 190—192°. The salts are, as a rule, very soluble, and of a gummy character. The acid contains a lactone group, and combines with one molecule of potash in the cold, two on heating. It was found impossible to obtain the free bibasic acid, *hydroxydiaterpenylic acid*, $COOH \cdot CH_2 \cdot CH(CMe_2 \cdot OH) \cdot CH(OH) \cdot COOH$, by decomposing the salts formed by dissolving hydroxyterpenylic acid in alkalis, but its

silver salt, $C_8H_{13}Ag_2O_6$, was obtained in the form of a white precipitate. Hydroxyterpenylic acid is easily reduced by hydriodic acid to terpenylic acid, melting at $55-56^\circ$. *Methylic hydroxyterpenylic acid*, $C_8H_{14}O_6$, cannot be prepared by the etherification of the acid, but may be obtained by the action of methylic iodide on the silver salt; it is a thick, colourless oil. This same methylic salt is also formed when the silver salt of the bibasic hydroxydiaterpenylic acid is treated in the cold with methylic iodide.

When hydroxyterpenylic acid is distilled at a pressure of 10 mm. or treated with alcohol and hydrochloric acid, it yields a *dilactone*, $CO < \begin{smallmatrix} CH_2 \cdot CH \cdot CMe_2 \\ O - CH - CO \end{smallmatrix} > O$, melting at 129° ; this substance requires one molecule of potash for neutralisation in the cold, but two on heating. When the solution in one molecule of potash is acidified, however, the dilactone itself is reproduced and not hydroxyterpenylic acid. With two molecules of potash, the salts of hydroxydiaterpenylic acid are formed. These results are best explained (compare Schryver, *Trans.*, 1893, 1327) by ascribing the formulæ given above to these derivatives.

A. H.

Citric acid and its Alkali Salts. By T. SALZER (*Arch. Pharm.*, 231, 514—521; compare Abstr., 1892, 149).—Finely powdered citric acid becomes anhydrous when slowly heated at 55° , and in this condition melts at 160° . Buchner and Witter (Abstr., 1892, 824) have shown that anhydrous citric acid may be regenerated from its lead salt by decomposing it with hydrogen sulphide, whilst the corresponding lead salt obtained from the hydrated acid gives rise to the modification from which it is derived. On examining the sodium and potassium salts derived from the anhydrous acid, however, the author finds that they are identical with those of the hydrated form.

Monosodium citrate prepared from the anhydrous acid crystallises with $1H_2O$, and dissolves in about $4\frac{1}{2}$ parts of water at 18° and $1\frac{1}{2}$ parts at 100° , being slightly more soluble than the anhydrous salt. The disodium citrate described by Heldt is monohydrated, but the author's investigation points to the existence of a salt crystallising with $2\frac{1}{2}H_2O$, and soluble in about 3 parts of cold water; the greater part of the water of crystallisation is driven off at 100° .

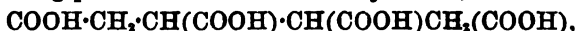
Anhydrous monopotassium citrate (Abstr., 1892, 149) can be obtained in measurable crystals belonging to the triclinic system.

M. O. F.

Stereoisomeric Butanetetracarboxylic acids. By K. AUWERS and A. JACOB (*Ber.*, 27, 1114—1132; compare Abstr., 1893, i, 253).—If ethylic sodiomalonate is allowed to react with ethylic aconitate in benzene solution, and if not more than 1 atom of sodium is present for each molecule of the malonate, then no ketopentamethylenedicarboxylate is formed, as when alcohol is employed as a solvent, but a mixture is obtained from which only the two acids melting at 185° and 244° (more correctly 189° and 232°) can be isolated. These are shown to be stereochemically isomeric butanetetracarboxylic acids, and are distinguished by the letters *h* and *n* prefixed respectively to the acid of higher and of lower (*niedriger*) melting point. Each acid

yields ethereal salts and anhydrides, and the members of the two series are interconvertible, as appears below.

The starting point is *n*-butanetetracarboxylic acid,



melting at 189°. The product of the above-mentioned action is heated with hydrochloric acid, the crystals of the two acids collected, dried, and boiled with acetic anhydride, when, from both acids, the anhydride of the *n*-acid is formed. From the latter, by dissolving it in water and crystallising, the *n*-acid can itself be obtained. The *tetramethylic*, *diethylic*, and *dipropylic* salts melt at 75–76°, 168°, and 129°; the *tetrethylic* salt, which, unlike the others, was prepared by the aid of heat, is an oil boiling at about 300°. The acid itself, in acetic acid solution, has an abnormal molecular weight (=153) as determined cryoscopically; its sodium salt, like that of its isomeride, exhibits a much smaller dissociation in solution than is the case with other tetracarboxylic acids. When the acid is heated to boiling with a large excess of acetic anhydride, it is immediately converted into the *n*-dianhydride, $\text{C}_8\text{H}_4\text{O}_8$; this crystallises in small octahedra with adamantine lustre, softens at 245°, and melts at 248°, is attacked only very slowly by sodium carbonate in the cold, and gradually absorbs moisture, becoming reconverted into the acid. If the *n*-acid is heated at 190° with nitrobenzene, it yields the *h*-mono-anhydride, $\text{C}_8\text{H}_6\text{O}_7$; this forms small, nacreous plates, softens at 228°, and melts and decomposes at 232°. Cold water hardly dissolves it, but boiling water converts it into *h*-butanetetracarboxylic acid, which melts at 236°, and is less soluble in water than the *n*-acid; the *tetramethylic* salt of this acid melts at 63–64°. When this acid is heated for two days with acetic chloride at 100° in a sealed tube, it yields the *h*-dianhydride, which melts at 168° (not at 172–173°, as previously given), and is readily attacked by sodium carbonate. It can be converted into the *n*-isomeride by boiling it for a few minutes with nitrobenzene.

C. F. B.

Urethane. By A. HANTZSCH (*Ber.*, 27, 1248–1254).—*Dichlor-ethylenurethane*, $\text{CCl}_2\text{C}:\text{N}\cdot\text{COOEt}$, is prepared by the action of sodium ethoxide on anhydrochloralurethane, $\text{CCl}_2\cdot\text{CH}:\text{N}\cdot\text{COOEt}$ (*Abstr.*, 1891, 1003), and crystallises from alcohol in stellate needles melting at 37°. It is readily volatile with steam, and has an odour of carnations. Urethane and glyoxalic acid yield a compound



crystallising in colourless needles which melt at 156°. The condensation product of urethane and trichloroacetic cyanide is oily; with paranitraniline the cyanide combines to form *trichloroacetoparanitranilide*, $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, which is crystalline, and melts at 142°. Urethane and benzaldehyde, in presence of sodium ethoxide, yield benzylidenediurethane.

Oxalyldiurethane, $\text{C}_2\text{O}_3(\text{NH}\cdot\text{COOEt})_2$, is prepared from ethylic oxalate and urethane in presence of sodium ethoxide; it is crystalline, and melts at 170°. Ethylic salts of the fatty acids do not combine with urethane.

Ethylic dibromamidocarboxylate sodium bromide, $4\text{NBr}_2\cdot\text{COOEt} + \text{NaBr}$, is formed by the action of bromine and soda on urethane, as a yellow, granular powder; the sodium bromide is not removed by washing with water; it melts and decomposes at 136° , and also decomposes slowly at ordinary temperatures in presence of moisture. The yield is almost quantitative. The *potassium salt* closely resembles the sodium compound; both react violently with ammonia or ammonium carbonate. By the action of ether, carbon bisulphide, or chloroform on the salts, *ethylic dibromamidocarboxylate* is obtained; this is a yellowish-red, unstable oil, has a penetrating odour, and reacts with anhydrous ammonia to form nitrogen and urethane. By the action of sodium amalgam on the preceding compound, or on the additive product, a complex reaction takes place resulting in the formation of *bromethylidenediurethane*, $\text{CH}_2\text{Br}\cdot\text{CH}(\text{NH}\cdot\text{COOEt})_2$, which crystallises in colourless needles, melts at $142\text{--}143^\circ$, and closely resembles the corresponding chloro-derivative. On boiling with dilute hydrochloric acid, it is resolved into bromaldehyde and urethane. *Ethylic dibromamidocarboxylate* therefore reacts with ether like free bromine, converting it into bromaldehyde, which then, in presence of hydrogen bromide, condenses with the urethane. *Dibromethylidenediurethane*, $\text{CHBr}_2\cdot\text{CH}(\text{NH}\cdot\text{COOEt})_2$, is formed by the decomposition of ethylic dibromamidocarboxylate in presence of moisture; it is crystalline, and, like the dichloro-compound, melts at 120° .

J. B. T.

Hydroxyurethane and certain reactions of Benzhydroxamic acid. By A. HANTZSCH (*Ber.*, 27, 1254—1257).—Ethylic carbonate reacts less readily with hydroxylamine than the ethylic salts of fatty acids. *Hydroxyurethane*, $\text{OH}\cdot\text{NH}\cdot\text{COOEt}$ or $\text{OH}\cdot\text{C}(\text{OEt})\cdot\text{NOH}$, is prepared by the interaction of hydroxylamine hydrochloride and ethylic carbonate in aqueous solution with soda, or, better, in alcoholic solution with sodium ethoxide; the yield is increased if ethylic chlorocarbonate is substituted for the ethylic carbonate. It is a colourless, odourless liquid, miscible in all proportions with water, yields a dark violet coloration with ferric chloride, and is more stable towards acids than the true hydroxamic acids; alkaline copper solution is only reduced by prolonged boiling and evaporation with hydrochloric acid. The *copper salt* is green and slimy.

The following experiments had for their object the conversion of hydroxamic acids, $\text{OH}\cdot\text{CR}\cdot\text{NOH}$, into anhydrides, $\text{RC}\begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$. *Hydroxyurethane*, if heated with phosphorous pentachloride, but not with phosphoric anhydride, yields a yellow oil which is not an anhydride but probably the chloro-derivative $\text{OEt}\cdot\text{CCl}\cdot\text{NOH}$. *Benzhydroxamic acid acetate*, $\text{OH}\cdot\text{CPh}\cdot\text{NOAc}$, is relatively stable, and crystallises from water; it melts 1° higher than the acid, and, on strongly heating, yields phenylic isocyanate. On gently warming with potash, it is hydrolysed yielding benzhydroxamic acid, but, with potassium carbonate, diphenylcarbamide and some aniline are formed; this reaction resembles that of benzaldoxime acetate, and is not given by benzhydroxamic acid; in all probability the anhydride $\text{CPh}\begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ is first

formed, then, by intramolecular rearrangement, phenylic isocyanate, which reacts with the water to form diphenylcarbamide.

J. B. T.

Amidosulphonic acids. By C. PAAL and F. KRETSCHMER (*Ber.*, 27, 1241—1247).—*Ethyllic amidosulphonate*, $\text{NH}_2\cdot\text{SO}_2\cdot\text{Et}$, is obtained from ethylic iodide and silver amidosulphonate as an oily liquid, which decomposes on distillation; it is completely miscible with water or alcohol, and by the action of water or of alcoholic ammonia is converted into ammonium ethylic sulphate. The silver salt, $\text{NH}_2\cdot\text{SO}_2\cdot\text{Ag}$, has recently been prepared by Eitner, and crystallises in colourless, lustrous needles. The *copper salt* crystallises in small, blue, the *lead salt* in colourless, needles. The *aniline salt*, $\text{NH}_2\cdot\text{SO}_2\cdot\text{NH}_2\cdot\text{Ph}$, is prepared by mixing the constituents in warm aqueous solution, and is deposited in large, colourless plates; it melts at $148\text{--}149^\circ$, and is slowly decomposed by prolonged heating in aqueous or alcoholic solution.

Ammonium anilidosulphonate, $\text{NHPh}\cdot\text{SO}_2\cdot\text{NH}_4$, is prepared by boiling the acid with aniline (5—6 parts), and crystallises from dilute alcohol in colourless plates which blacken at high temperatures.

Phenylhydrazine amidosulphonate, $\text{NH}_2\cdot\text{SO}_2\cdot\text{NH}_2\cdot\text{NHPh}$, prepared like the aniline salt, crystallises in large, colourless needles, and melts at 124° . *Ammonium phenylhydrazidosulphonate*,



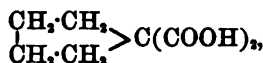
is obtained in a similar manner to the aniline derivative; it crystallises from alcohol in colourless, lustrous, flat needles, melts at 208° with decomposition, and, in aqueous solution, gives a light-grey precipitate with mercuric chloride, and a metallic mirror with silver nitrate. The yield is quantitative.

Ammonium benzeneazosulphonate, $\text{NPh}\cdot\text{N}\cdot\text{SO}_2\cdot\text{NH}_4$, is formed by the oxidation of the preceding compound by means of mercuric oxide; it crystallises in yellow plates, or flat needles, and melts and decomposes at 205° . The *potassium* and *sodium salts* crystallise in yellow plates. The *silver salt*, $\text{N}_2\cdot\text{Ph}\cdot\text{SO}_2\cdot\text{Ag}$, is deposited in gold-coloured plates, and explodes on heating. The *ethylic salt* is unstable, and was obtained as a dark-red, viscid liquid. The *free acid* has only been prepared in solution, and readily decomposes. The preceding sulphonic acid derivatives of phenylhydrazine and aniline are probably not formed directly, but are either produced from the salts by the elimination of water and subsequent action of this water on the diamide $\text{NH}_2\cdot\text{SO}_2\cdot\text{NH}_2\cdot\text{R} = \text{NH}_2\cdot\text{SO}_2\cdot\text{NHR} + \text{H}_2\text{O} = \text{NH}_4\cdot\text{SO}_2\cdot\text{NHR}$; or they are formed by the elimination of ammonia and its combination with the free sulphonic acid, thus $\text{RNH}_2 + \text{NH}_2\cdot\text{SO}_2\cdot\text{H} = \text{RNH}\cdot\text{SO}_2\cdot\text{H} + \text{NH}_3 = \text{RNH}\cdot\text{SO}_2\cdot\text{NH}_4$ ($\text{R} = \text{C}_6\text{H}_5$, or NHPh). As no intermediate products have been isolated, it is impossible to distinguish between these theories.

J. B. T.

Synthesis of Pentamethylenecarboxylic acid. By W. STAUSS (*Ber.*, 27, 1228—1230).—The pentamethylenecarboxylic acid, prepared by Gärtner (*Annalen*, 275, 331) from ketopentamethylene by

means of hydrocyanic acid, can also be obtained by the action of tetramethylene dibromide on ethylic malonate in the presence of sodium ethoxide. The pentamethylenedicarboxylic acid,



obtained by the hydrolysis of the product, melts at 176—178°, and loses the elements of carbonic anhydride. The monobasic acid thus produced is identical with Gärtner's acid.

Note.—The author has overlooked the fact that Haworth and Perkin (*Trans.*, 1894, 86) have carried out the synthesis of pentamethylenedicarboxylic acid in precisely the way indicated in the foregoing paper. A. H.

Synthesis of Hexahydrobenzoic acid. By H. BUCHERER (*Ber.*, 27, 1230—1232).—Ketoexamethylene reacts with hydrocyanic acid in a similar manner to ketopentamethylene (*Annalen*, 275, 333), first the nitrile, and from that by hydrolysis *α*-hydroxyhexamethylene-carboxylic acid, $\text{CH}_2 < \begin{array}{c} \text{CH}_2\text{CH}_2 \\ | \quad | \\ \text{CH}_2\text{CH}_2 \end{array} > \text{CH}(\text{OH})\cdot\text{COOH}$, being produced.

This substance is soluble in 14 parts of water, readily soluble in alcohol, ether, and benzene, and crystallises in colourless plates, or from aqueous solution in thick prisms with a vitreous lustre, and melts at 106—107°. The calcium salt, $\text{C}_{14}\text{H}_{22}\text{CaO}_6 + 3\text{H}_2\text{O}$, and silver salt are both crystalline. When heated at 190—200° with phosphorus and hydriodic acid, the free acid is converted into hexahydrobenzoic acid. A. H.

Constitution of Benzene. By J. W. BRÜHL (*J. pr. Chem.*, [2], 49, 201—294, and *Ber.*, 27, 1065—1083).—The author discusses at length our present views on the constitution of benzene, and concludes that Kekulé's formula, in which three double bonds are supposed to exist in the benzene ring, is in closer agreement with the facts than Claus's diagonal formula which is supported by v. Baeyer (*Abstr.*, 1892, 1211).

Substance.	<i>d</i> at 20°/4°.	Mol. vol. at 20°.	$\frac{P \cdot n^2 - 1}{d(n^2 + 2)}$.	
			For H_2 .	For D.
Benzene, C_6H_6	0·8799	88·65	25·93	26·13
Dihydrobenzene, C_6H_8	0·8478	94·36	26·33	26·61
Tetrahydrobenzene, C_6H_{10}	0·8102	101·21	26·87	27·01
Hexahydrobenzene, C_6H_{12}	0·780	107·2	27·56	27·66
Hexane, C_6H_{14}	0·6603	130·25	29·70	29·84
Hexylene, C_6H_{12}	0·6825	128·08	29·45	29·61
Diallyl, C_6H_{10}	0·6880	119·18	28·77	28·86
Dipropargyl, C_6H_6	0·8049	96·91	25·57	25·74

The molecular volumes and refraction constants of benzene, and of several hydrogenated benzenes and six-carbon atoms open-chain hydrocarbons were determined; the results are tabulated on p. 366.

The numbers obtained for the densities decrease slowly as the degree of hydrogenation of the benzene nucleus increases; considerable difference exists, however, between the density of hexahydrobenzene and that of hexane. The density slowly increases from hexane to diallyl, and then, in going from diallyl to dipropargyl, a great increase occurs. The molecular volumes change in much the same way. The change in molecular volume which occurs on passing from one hydrocarbon to another is even more marked than the change of density. Large differences in specific refraction also exist between hexahydrobenzene and hexane, and between diallyl and dipropargyl; the molecular refractions for the rays H_α and D change in an analogous manner, as is seen on inspecting the table. In the complete paper, a table of the molecular and specific dispersions between H_γ and H_α is given, from which it is seen that these constants also exhibit sudden changes at the points mentioned above.

The large changes in physical properties observed on passing from hexahydrobenzene to hexane, and from diallyl to dipropargyl, are evidently due, in the first case, to the opening of the ring, and, in the second, to the change of an ethylenic bond to an acetylenic one. No large change in any of these properties is observed in the passage from benzene to dihydrobenzene, as would be expected if the molecular structure of benzene materially differed from that of its dihydro-derivative. The hypothesis that benzene possesses a cyclic or a diagonal constitution, is consequently opposed to the facts, and it must be concluded that benzene contains three ethylenic bonds, dihydrobenzene two, and the tetrahydro-derivative one only. The molecular refractions calculated for all the above hydrocarbons on these assumptions, are in close agreement with those observed. According to v. Baeyer, the benzene nucleus in phthalic acid should contain three diagonal bonds; the observed molecular refraction of ethylic phthalate is, however, 58.20 for the ray H_α , whilst the value, calculated on v. Baeyer's assumption, is only 51.79. The value calculated from the Kekulé formula is 57.30, a number which agrees fairly well with that observed. Benzene and phthalic acid are, consequently, not representatives of a desmotropic ring system, and the benzene nucleus cannot exist in two tautomeric forms, but always has the constitution indicated by the Kekulé formula.

The author considers that the thermochemical data for benzene derivatives, obtained by Stohmann (this vol., ii, 80), and supposed by him to be evidence strongly supporting the views of v. Baeyer, are in complete accordance with Kekulé's benzene formula. Stohmann's work, and also that of v. Baeyer, is discussed at length.

The arrangement in space of the atoms constituting the benzene molecule is best grasped by the use of Sachse's models.

W. J. P.

New Mode of Formation of Nitrosobenzene. By E. BAXBERGER and B. BERLÉ (*Ber.*, 27, 1182).—It has hitherto been stated,

that when azoxybenzene is heated, aniline and azobenzene are produced. The authors find that if the heating is carried out slowly, small quantities of nitrosobenzene are also formed. L. T. T.

Action of Sulphuryl Chloride on the Phenols and their Ethers. By A. PERATONER and F. FINOCCHIARO (*Gazzetta*, 24, i, 236—246; compare Töhl and Eberhart, this vol., i, 132).—The authors confirm Dubois' statement (*Zeits. Chem.*, 1866, 705) that parachlorophenol is the only product of the action of sulphuryl chloride on phenol, either solid or in chloroform solution.

Sulphuryl chloride has no action on boiling anhydrous ethereal solutions of phenylic benzoate, dibenzoylresorcinol, or triacetylphloroglucinol, although in the latter case a little free phloroglucinol is formed, probably owing to the presence of moisture. On boiling an anhydrous ethereal solution of diacetylresorcinol with sulphuryl chloride, a small quantity of a derivative containing chlorine in the acetyl-group is obtained; its nature could not be more exactly determined.

Trichlorophloroglucinol is obtained by the action of sulphuryl chloride on phloroglucinol in ethereal solution; it melts at 133—134°, not at 129° as stated by Hazura and Benedikt (*Abstr.*, 1886, 52).

W. J. P.

Action of Halogens on Homocatechol. By H. COUSIN (*Compt. rend.*, 118, 809—811).—When chlorine is passed into a solution of homocatechol in glacial acetic acid until it begins to acquire a red colour, trichlorohomocatechol, $C_7H_5Cl_3O_2$, is formed, and crystallises from dilute acetic acid containing a small quantity of sulphurous acid in slender, white needles, which rapidly become brown on exposure to light. It is insoluble in water, but dissolves in alcohol, ether, and boiling acetic acid. The crystals are hydrated, but lose their water in a dry vacuum, and the anhydrous compound melts at 179—180°.

Longer action of chlorine on the acetic acid solution of homocatechol yields a dark red solution, which, on cooling, deposits bright red, crystalline lamellæ of the compound $C_7H_5Cl_3O_2$, a dehydration product analogous to that obtained by Zincke from tetrachlorocatechol. The same product is obtained by the action of a mixture of concentrated nitric acid and glacial acetic acid on a solution of trichlorohomocatechol in a small quantity of absolute alcohol. It can be recrystallised from hot acetic acid, and also dissolves in alcohol and ether, but is insoluble in water; it melts at 97—98°.

The prolonged action of chlorine yields pale yellow, higher chlorine derivatives, which have not yet been fully investigated.

When bromine is added gradually to homocatechol until it is no longer absorbed, there is an energetic action, and when the product is repeatedly crystallised from acetic acid containing a small quantity of sulphurous acid, the tribromo-derivative, $C_7H_5Br_3O_2$, is obtained in long, silky, white needles, which become brown when exposed to light; it melts at 162—164°, and is insoluble in water, but dissolves in alcohol, ether, and acetic acid. With excess of bromine, homocatechol yields a red product, analogous to the chlorine compound; it is more easily obtained by the action of nitric acid, and crystallises

from hot acetic acid in large, garnet-red lamellæ, which melt at 117—118°. When dissolved in alcohol and heated with sulphurous acid, the compound $C_7H_5Br_3O_2$ is regenerated.

Prolonged action of bromine on homocatechol yielded no substitution products higher than the tribromo-derivative.

Iodine, under various conditions, yields no iodo-derivatives with homocatechol.

C. H. B.

Derivatives of Orthoamidobenzyllic Alcohol. By C. PAAL and H. SENNINGER (*Ber.*, 27, 1084—1087).—The authors have continued the investigation (*Abstr.*, 1893, i, 23) of orthoamidobenzyllic alcohol and its derivatives. The alcohol yields orthotoluidine on reduction with metallic sodium in alcoholic solution, and gives saligenin when treated with nitrous acid.

Orthoamidobenzyllic alcohol hydrogen oxalate, $C_7H_5NO, H_2C_2O_4$, crystallises in white needles, melting at 130°, and is soluble in water or hot alcohol. The *picrate*, $C_7H_5NO, C_6H_3N_3O_7$, is obtained in slender, yellow needles, melting at 110°.

Diazobenzyllic alcohol hydrogen sulphate, $OH \cdot CH_2 \cdot C_6H_4 \cdot N_2 \cdot HSO_4$, is obtained by diazotising the alcohol in the ordinary way with amyl nitrite and sulphuric acid; it crystallises in greenish needles, exploding at 50°, and is readily soluble in water. On diazotising the alcohol with sodium nitrite and hydrochloric acid, and adding a soda solution of resorcinol, the *sodium-derivative* of resorcinolorthoazobenzyllic alcohol is obtained in red, microcrystalline flocks. The free *azo-compound*, $C_6H_3(OH)_2 \cdot N_2 \cdot C_6H_4 \cdot CH_2 \cdot OH$, crystallises in red needles, melting at 170°. The α -*naphtholazo-compound* crystallises in leaflets melting at 182°, whilst the β -*naphtholazo-compound* is obtained in brown needles, melting at 185°. Similar compounds with phenol and dimethylaniline were prepared, although not in a pure state.

On boiling orthoamidobenzyllic alcohol with epichlorhydrin, a *chlorohydroxypropylamidobenzyllic alcohol*, $C_{10}H_{11}ClNO_2$, is obtained; it forms white needles, melting at 95°, and is readily soluble in the ordinary organic solvents.

W. J. P.

Relationships between Nitrosamines, Diazo-acids, and Isodiazocompounds. By E. BAMBERGER (*Ber.*, 27, 1179—1182).—The direct conversion of isodiazosalts into nitrosamines of secondary bases has been recently effected (Schmitt and Schraube, this vol., i, 237, and Bamberger, *ibid.*, 295). The author has now succeeded in reversing this action. Methylphenylnitrosamine, when dropped on to fused potash, is rapidly oxidised, with formation of isodiazobenzene. Similarly, β -naphthylnitrosamine and benzylmethylnitrosamine yield the corresponding isodiazosalts. Benzenediazoic acid, when treated with 8 per cent. sodium amalgam, is partially reduced to isodiazobenzene.

L. T. T.

Action of Diazobenzene Chloride and its Homologues on Ethylic Cyanacetate. By F. KRÜCKEBERG (*J. pr. Chem.*, [2], 49, 321—354; compare *Abstr.*, 1893, i, 210, 509).—The ethylic salts of azo-aromatic cyanacetic acids can be obtained in a stable (β) and an

unstable (α) modification. The former is produced when the aqueous solution of the potassium compound is decomposed by carbonic anhydride, the latter when a mineral acid or acetic acid is used to effect the decomposition. The α -form generally passes into the β -form when heated either alone or in alcohol.

Ethyl *carboxyethylazobenzenecyanacetate* (Abstr., 1893, i, 509) crystallises in white needles and melts at 107° ; when warmed with alcoholic potash, the carboxethyl group is replaced by potassium. *Ethylazobenzenecyanacetamide*, $\text{N}_2\text{Ph}\cdot\text{CEt}(\text{CN})\cdot\text{CONH}_2$, is the product of the action of alcoholic ammonia on ethyl *ethylazobenzenecyanacetate*; it is nearly colourless, and melts at 155° . The benzoyl (Abstr., 1893, i, 210) and carboxethyl derivatives yield *azobenzenecyanacetamide* (m. p. 245° , *loc. cit.*) under similar treatment.

Azobenzenecetamide, $\text{N}_2\text{HPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$, is the product of the action of aqueous potash on ethyl *azobenzenecyanacetate*; it crystallises in yellowish needles, and melts at 178° . The corresponding acid is identical with Elber's phenylhydrazineglyoxylic acid (Abstr., 1885, 535).

By passing nitrous anhydride into a cooled benzene solution of either α - or β -ethyl *azobenzenecyanacetate*, a compound, apparently $\text{N}_2\text{HPh}\cdot\text{C}(\text{CN})\cdot\text{COOEt}\cdot\text{N}_2\text{O}_3$, is obtained in white crystals, which soon become brown in air, and explode at 70° . This substance does not give Liebermann's reaction, and phenol is a product of its distillation with water. When alcohol or ether is used as the solvent, this compound is not produced. If, during the passage of the nitrous anhydride through the benzene solution, the temperature rises to that of the room, a different compound, possibly $\text{NO}\cdot\text{NPh}\cdot\text{N}\cdot\text{C}(\text{CONH}_2)\cdot\text{COOEt}$, is formed; this crystallises in slender, green needles, melts at 178° , and dissolves freely in benzene, but only sparingly in ether, light petroleum, or water; it does not give Liebermann's reaction.

Iodine in aqueous solution converts α -ethyl *azobenzenecyanacetate* into the β -modification. Bromine yields a *dibromo*-derivative, which crystallises in laminæ, melts at 166° , and dissolves freely in benzene, glacial acetic acid, and alcohol, more sparingly in ether and light petroleum, but not in water.

Ethyl α -*azorthotoluenecyanacetate* (Abstr., 1893, i, 509) crystallises in yellow rhombohedra, melts at 85° , and dissolves to the extent of 24.57 parts in 100 of benzene at 19° . It is readily transformed into the more stable β -form when heated above its melting point. The β -modification melts at 133° , and dissolves to the extent of 5.7 parts in 100 of benzene at 19° . Thus the higher melting point and lower solubility belong to the stable form of the orthotoluene derivative, but to the unstable form of the benzene derivative. By hydrolysis with alcoholic potash, the ethyl salt yields the corresponding *acid*, which decomposes and melts at 173° .

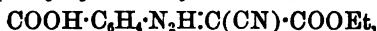
Ethyl α -*azoparatoluenecyanacetate* (*loc. cit.*) melts at 116 — 118° ; 9.74 parts of it dissolve in 100 of benzene at 20° . The β -modification melts at 74 — 75° , and dissolves in benzene at 20° to the extent of 53.65 parts in 100.

Ethyl *azometazylenecyanacetate*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}_2\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$. The stable β -form crystallises in yellow prisms and melts at 166° ; 3.61

parts dissolve in 100 of benzene at 18°. The unstable α -form crystallises in yellow prisms, melts at 74–75°, and dissolves to the extent of 25·00 parts in 100 of benzene at 18°.

Ethylic azopseudocumenecyanacetate, from diazopseudocumene chloride and ethylic cyanacetate. The β -form melts at 136°, the α -form at 100°; both forms are freely soluble in alcohol, ether, and benzene, and crystallise in slender needles. The corresponding *acid* crystallises in long prisms, and melts at 184°.

Ethylic carboxyphenylhydrazonocyanacetate,



from ethylic cyanacetate and diazobenzene hydrochloride, crystallises in slender needles and melts at 215°.

Formulæ are given, showing how the α - and β -modifications of these ethylic salts may be (1) stereoisomerides, (2) tautomerides, or (3) isomerides formed by migration of a hydrogen atom. A. G. B.

Acetoacetanilide. By L. KNORR and B. REUTER (*Ber.*, 27, 1169–1177).—*Acetoacetanilide* is prepared by the interaction of ethylic acetoacetate and aniline at 130–140° and crystallises from water in colourless plates melting at 85°. The yield is more than one-third of the theoretical. The *oxime*, $\text{NOH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, is formed at ordinary temperatures, crystallises from alcohol in needles, and melts at 125°. It is readily soluble in alkalis, insoluble in dilute acids, and gradually decomposes spontaneously. On heating with glacial acetic acid, or soda, or by the action of sulphuric acid, the *oxime* is converted into methylisoxazolone, $\text{CMe}\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{smallmatrix} \text{CH}_2$ (compare Hantzsch, *Abstr.*, 1891, 739).

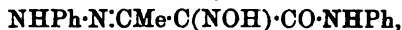
The *dioxime*, $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NOH})\cdot\text{CO}\cdot\text{NHPh}$, is prepared by gently heating the *oxime* with hydroxylamine hydrochloride, and crystallises from alcohol in yellow plates melting at 192°. It readily dissolves in alkalis, is precipitated by acids, and on heating with phenylhydrazine in acetic acid solution, 1-phenyl-3-methyl-4-keto-5-pyrazolone phenylhydrazone, $\text{CMe}\begin{smallmatrix} \text{N} \text{---} \text{NPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{N}\cdot\text{NHPh}) \end{smallmatrix} \text{CO}$, is formed; this compound is obtained in a similar manner from methylketoisoxazolone phenylhydrazone (see below), diphenylhydrazineacetylgyoxalic acid being formed in both cases as an intermediate product.

Acetoacetanilide ketophenylhydrazone, $\text{NHPh}\cdot\text{N}\cdot\text{CAc}\cdot\text{CO}\cdot\text{NHPh}$, is prepared by the action of diazobenzene chloride on acetoacetanilide; it crystallises from alcohol in pale yellow needles, and melts at 98–99°.

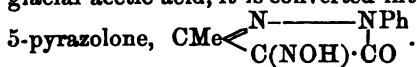
Acetoacetanilide phenylhydrazone, $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, is formed from phenylhydrazine and the anilide; it crystallises from alcohol in plates, melts at 128°, and gives an intense cherry colour with sulphuric acid. The yield is 75 per cent. of the theoretical. On boiling with soda or glacial acetic acid, it is converted into 1-phenyl-3-methyl-5-pyrazolone, which was identified by the formation of pyrazole-blue.

Acetylgyoxalanilide diphenylhydrazone,

from the phenylhydrazone by the action of diazobenzene chloride or from phenylhydrazine and the ketohydrazone, crystallises from alcohol in needles, melts at 173—175°, and, on heating with glacial acetic acid, is converted into methylketopyrazolone phenylhydrazone (see preceding page).

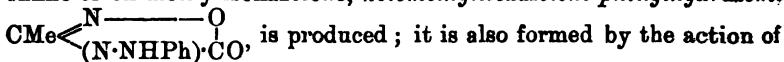
Acetylgyoxalanilide oximephenylhydrazone,

is prepared from the isonitroso-derivative and phenylhydrazine, and crystallises, with 1 mol. alcohol, in yellow needles melting at 181°. the alcohol-free compound melts at 168—169°. On boiling with glacial acetic acid, it is converted into 1-phenyl-3-methyl-4-isonitroso-

*Acetylgyoxalanilide phenylhydrazonoxime,*

is formed from the ketohydrazone and hydroxylamine hydrochloride; it crystallises from alcohol in thin plates, and melts at 175° with decomposition.

By the interaction of diazobenzene chloride and acetoacetanilide oxime or on methylisoxazolone, *ketomethylisoxazolone phenylhydrazone.*

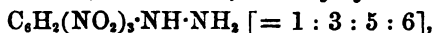


nitrous acid on the oxime, and by the hydrolysis of acetylgyoxalanilide hydrazonoxime; it crystallises from alcohol in yellow plates, melts and decomposes at 189°, and, on treatment with phenylhydrazine, is converted into acetylgyoxalic acid diphenylhydrazone, $\text{NPh}\cdot\text{N}:\text{CMe}\cdot\text{C}(\text{N}\cdot\text{NPh})\cdot\text{COOH}$ (m. p. 212°). Phenyl-

methylisotriazolecarboxylic acid, $\text{CMe} \begin{array}{c} \text{N} \text{---} \text{NPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{COOH}) \end{array} \text{N}$, has been previously prepared by Pechmann, and is obtained by heating acetylgyoxalanilide oximehydrazone with potash at 140—150°, acetylgyoxalic acid hydrazonoxime is formed as an intermediate product.

J. B. T.

Action of Picrylic Chloride on Hydrazine Hydrate. By A. PURGOTTI (*Gazzetta*, 24, i, 112—116).—*Picrylhydrazine,*



is obtained by boiling a mixture of caustic potash, hydrazine sulphate, and picrylic chloride in alcoholic solution; water must be present in order that the yield of the product should be good. It crystallises in brown, transparent, monosymmetric crystals, and melts and decomposes at 173°. It is soluble in ethylic acetate; it reduces Fehling's solution and ammoniacal silver nitrate. On boiling with benzaldehyde, it yields a golden-yellow, crystalline substance melting at 252°.

W. J. P.

Reduction of Nitro-compounds. By E. BAMBERGER (*Ber.*, 27, 1347—1350).—The author finds that when nitrobenzene is boiled for a short period with water and zinc dust, β -phenylhydroxylamine, $\text{NHPH}\cdot\text{OH}$, separates from the filtrate in long, colourless needles; it melts at $80\text{--}81^\circ$, and is characterised by its sensitiveness towards alkalis, which instantaneously decompose it, as well as by its great reducing power. It is readily converted into nitrosobenzene on oxidation, and into paramidophenol by mineral acids. Nitromethane when boiled with zinc dust and water, yields methylhydroxylamine without recognisable quantities of methyamine or ammonia; in a similar manner, nitric acid and nitrous acid yield not inconsiderable amounts of hydroxylamine on reduction with zinc dust and water. (Compare, however, Wohl, *Ber.*, 27, 1432; Bamberger, *ibid.*, 1547.)

A. R. L.

Blue Coloration Produced by the Action of Acids on Leucauramines. By A. ROSENSTIEHL (*Compt. rend.*, 118, 741—743).—Graebe observed that when leucauramine is treated with acids, a blue coloration is produced, and he assumed that this compound is capable of existing in two isomeric modifications, one colourless, the other coloured. The coloration is fugitive with hydrochloric acid but permanent with acetic acid. The author has observed, however, that a precisely similar coloration is obtained by the action of acids on diamidotetramethylbenzhydrol, which has a constitution similar to that of leucauramine. If the group $\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ is represented by A_2 , leucauramine is $\text{A}_2\cdot\text{CH}\cdot\text{NH}_2$, whilst diamidotetramethylbenzhydrol is $\text{A}_2\cdot\text{CH}\cdot\text{OH}$.

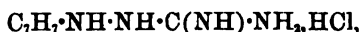
If leucauramine prepared by Graebe's method is dissolved in dilute hydrochloric acid, heated for 30 minutes on a water bath, and made alkaline with sodium hydroxide, a crystalline precipitate is obtained which contains 90 per cent. of diamidotetramethylbenzhydrol and 10 per cent. of unaltered leucauramine. When the benzhydrol is treated with an insufficient quantity of acid, the principal product is $\text{A}_3\cdot\text{CH}$, the leuco-base of hexamethylated Paris violet.

Leucauramine does not exist in the form of a blue modification, as Graebe supposed; the blue coloration is due to the formation of the chlorhydrin of diamidotetramethylbenzhydrol.

C. H. B.

Amidoguanidine and its Alkyl-derivatives. By G. PELLIZZARI and G. CUNEO (*L'Orosi*, 17, 73—89).—Amidoguanidine (compare Thiele, *Abstr.*, 1892, 1295) may be prepared by heating cyanamide with hydrazine hydrochloride in alcoholic solution.

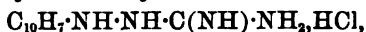
Orthotolylamidoguanidine hydrochloride,



is obtained by heating a mixture of orthotolylhydrazine hydrochloride and cyanamide or of phenylhydrazine hydrochloride and guanidine carbonate in alcoholic solution; it crystallises in large, red prisms and melts at 212° . The *nitrate* is obtained in beautiful, colourless needles melting at $206\cdot5^\circ$; the *platinochloride* forms magnificent yellow needles, and the *picrate* crystallises in large, yellow needles melting at 206° .

Paratolylhydrazine hydrochloride and cyanamide interact with formation of *paratolylamidoguanidine hydrochloride*; this crystallises in transparent scales and melts at 196.5° . The *nitrate* is obtained in transparent laminae melting at 181° , and the *platinochloride* forms beautiful, red crystals; the *picrate* crystallises in needles melting at 212° .

α-Naphthylamidoguanidine hydrochloride,

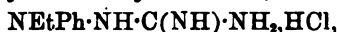


prepared by the action of cyanamide on *α-naphthylhydrazine hydrochloride*, separates from its aqueous solution in colourless crystals melting at 166° ; the *platinochloride* is a yellow, crystalline powder.

β-Naphthylamidoguanidine hydrochloride is obtained in minute, reddish crystals, which decompose at $250\text{--}260^{\circ}$; the *nitrate* is similar in appearance and melts at 230° . The *platinochloride* and *picrate* are coloured, crystalline powders.

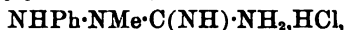
The bases whose salts are described above, could not be obtained in the free state; their salts immediately reduce ammoniacal silver nitrate but do not react with benzaldehyde.

Ethylphenylamidoguanidine hydrochloride,



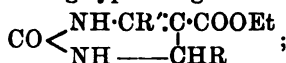
is obtained by boiling a mixture of *α-ethylphenylhydrazine hydrochloride* and cyanamide in alcoholic solution. The *platinochloride* forms a flocculent precipitate and melts and decomposes at 150° , whilst the *picrate* crystallises in hard, red prisms melting at 224° , and is accompanied by a small proportion of another *picrate* which separates in transparent scales melting at 269° .

Phenylamidomethylguanidine hydrochloride,



is prepared by the interaction of cyanamide and *β-phenylmethylhydrazine hydrochloride* in boiling alcoholic solution; it crystallises in small, colourless prisms and melts at 227° . The *platinochloride* crystallises in transparent, red needles, and the *nitrate* separates in white crystals melting at $105\text{--}106^{\circ}$; the *picrate* crystallises in yellow needles melting and decomposing at 215° . W. J. P.

Ethyllic Benzalbiuretamidocrotonate and Benzalbiuret. By P. BIGINELLI (*Gazzetta*, 24, i, 291—295).—The author has previously shown (*Abstr.*, 1893, i, 645) that carbamide interacts with an aldehyde and an acetoacetate or oxalacetate, water being eliminated; and a compound of the following type being formed,



it is now shown that a similar action occurs if other amides, such as biuret, are substituted for carbamide.

On boiling a mixture of biuret hydrate, benzaldehyde, and ethyllic acetoacetate with absolute alcohol, or on heating the mixture alone at 170° , water is formed, and a substance of the composition $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_5$ separates on cooling. It crystallises in tufts of small needles, melt-

ing at 184—185°, is soluble in hot alcohol, does not give the general reactions for biuret, and is hydrolysed by dilute acids or alkalis with liberation of benzaldehyde. It probably has the constitution

$$\text{CHPh}\cdot\text{NH}\cdot\text{CO}\text{---}\text{NH}\begin{matrix} > \\ > \end{matrix}\text{CO}, \text{H}_2\text{O}.$$

$$\text{C}(\text{COOEt})\cdot\text{CMe}\cdot\text{NH}\begin{matrix} > \\ > \end{matrix}\text{CO}, \text{H}_2\text{O}.$$

Ethyl benzalbiuretamidocrotonate may be prepared by the general method described in the paper referred to above; it therefore became of interest to attempt the preparation of compounds of biuret with aldehydes. On heating benzaldehyde with biuret hydrate at 170°, a product is obtained from which *benzalbiuret*, $\text{NH}\begin{matrix} > \\ > \end{matrix}\text{CO}\cdot\text{NH}\begin{matrix} > \\ > \end{matrix}\text{CHPh}$, may be isolated by washing with alcohol and water; it crystallises in small pyramids melting and decomposing at 272—273°, and is soluble in hot alcohol. It is not hydrolysed by dilute acids or alkalis in the cold, but, on boiling with concentrated potash, benzaldehyde is formed; ethylic acetoacetate has no action on it at 180°.

W. J. P.

Action of Aromatic Orthodiamines on some Anhydrides of Bibasic acids. By F. ANDERLINI (*Gazzetta*, **24**, i, 140—150).—Orthophenylenediamine and succinic anhydride in cold benzene solution yield an additive *product*, $\text{C}_6\text{H}_4(\text{NH}_2)_2\cdot\text{C}_4\text{H}_4\text{O}_3$, as a white deliquescent amorphous powder, which decomposes at 80°. On boiling with benzene or absolute alcohol, it decomposes with formation of *orthophenylenesuccinyldiimide*, $\text{C}_6\text{H}_4\begin{matrix} > \\ > \end{matrix}\text{NH}\cdot\text{CO}\begin{matrix} > \\ > \end{matrix}\text{NH}\cdot\text{CO}\begin{matrix} > \\ > \end{matrix}\text{C}_6\text{H}_4$; this crystallises in pearly scales melting and decomposing at 237°, and is soluble in alcohol or hot water.

Orthophenylenediamine combines with maleic anhydride in benzene solution to form an additive *product*, $\text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_2$, which separates from hot alcohol in small yellow, lustrous crystals melting and decomposing at 124—125°. On boiling with absolute alcohol, it yields a yellow, crystalline condensation *product* of complex composition melting and decomposing at 240°; another crystalline *product* melting at 168° is also formed.

The additive *product*, $\text{C}_6\text{H}_4(\text{NH}_2)_2\cdot\text{C}_6\text{H}_4\text{O}_3$, of orthophenylenediamine and phthalic anhydride, separates from hot alcohol as a yellow, crystalline mass melting at 144—155°. It yields *orthophenylenephthalalyldiimide*, $\text{C}_6\text{H}_4\begin{matrix} > \\ > \end{matrix}\text{NH}\cdot\text{CO}\begin{matrix} > \\ > \end{matrix}\text{NH}\cdot\text{CO}\begin{matrix} > \\ > \end{matrix}\text{C}_6\text{H}_4$, when boiled with absolute alcohol; this crystallises in white needles melting and decomposing at 278°, and is insoluble in water.

The additive *product*, $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2\cdot\text{C}_4\text{H}_4\text{O}_3$, obtained from orthotolylenediamine and succinic anhydride, is a hygroscopic, amorphous mass which decomposes at 90°; on heating at 100°, it yields *orthotolylenesuccinyldiimide*, $\text{C}_6\text{H}_3\text{Me}\begin{matrix} > \\ > \end{matrix}\text{NH}\cdot\text{CO}\begin{matrix} > \\ > \end{matrix}\text{NH}\cdot\text{CO}\begin{matrix} > \\ > \end{matrix}\text{C}_6\text{H}_3$, which crystallises in pearly-white scales melting and decomposing at 185—186°; it is soluble in hot water.

Orthotolylenediamine and maleic anhydride yield an additive *product*, $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2\cdot\text{C}_4\text{H}_4\text{O}_3$, but the condensation product could not be isolated.

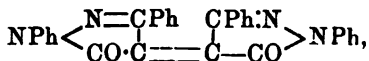
The additive product of orthotolylenediamine and phthalic anhydride, $C_6H_5Me(NH_2)_2, C_6H_4O_3$, is a crystalline powder which decomposes at 90° . On boiling its benzene solution, *orthotolylenephthalaldimide*, $C_6H_5Me < \begin{smallmatrix} NH \cdot CO \\ NH \cdot CO \end{smallmatrix} > C_6H_5$, is deposited; it forms a yellow, crystalline mass which softens at 140° .

W. J. P.

Ethyl: Phenylloxalacetate and Phenylmalonic acid. By W. WISLIZENUS (*Ber.*, 27, 1091—1095; compare this vol., i, 323).—Ethyl phenylloxalacetate, $COOEt \cdot CO \cdot CHPh \cdot COOEt$, was prepared in the manner described for the oxalacetate (*Abstr.*, 1888, 361). Its colourless *sodium* and green *copper derivatives* were prepared. From the former, by the action of dilute sulphuric acid, the ethylic salt itself was set free as a colourless oil; it was distilled under diminished pressure, when *ethylic phenylmalonate* was formed; the latter was purified by fractionation under diminished pressure. It is a colourless, odourless oil, boiling with slight decomposition at 285° ; under 14 mm. pressure, it boils at 170 — 172° . *Phenylmalonic acid*, $CHPh(COOH)_2$, melts at 152 — 153° , with evolution of carbonic anhydride and formation of phenylacetic acid. Its *sodium*, *calcium*, *silver*, and blue *copper* ($5H_2O$) *salts* were prepared.

C. F. B.

Action of Heat on Ethylic Dibenzoylsuccinate. By L. KNORR and M. SCHMIDT (*Ber.*, 27, 1167—1168).—Ethylic dibenzoylsuccinate is prepared in a similar manner to ethylic diacetosuccinate (compare this vol., i, 360); on heating at 270 — 290° , alcohol is eliminated, and a compound, $C_{18}H_{10}O_4$, is formed which is sparingly soluble, crystallises from ethylic acetoacetate in needles, melts at 288 — 289° , and sublimes without decomposition. It dissolves in concentrated sulphuric acid with a blue-violet colour; the yield is small. The compound appears to be a quinone, and although its constitution is uncertain, it is probably represented by one of the formulæ $C_6H_5 < \begin{smallmatrix} CO \cdot CH \cdot CO \\ CO \cdot CH \cdot CO \end{smallmatrix} > C_6H_5$; $C_6H_5 < \begin{smallmatrix} C(OH) \cdot C \cdot CO \\ C(OH) \cdot C \cdot CO \end{smallmatrix} > C_6H_5$; $C_6H_5 < \begin{smallmatrix} CO \text{---} C \cdot C(OH) \\ C(OH) \cdot C \text{---} CO \end{smallmatrix} > C_6H_5$. The mother liquor yields *bisdiphenylpyrazolone*,



which melts at 320° with decomposition, readily dissolves in alkalis, and is converted into a pyrazolone-blue on oxidation. Dibenzoyl-ethane (diphenacyl) is formed from ethylic dibenzoylsuccinate by warming it with soda (3 per cent.), or by heating with water at 150 — 170° , or with alcohol at 250° .

J. B. T.

Action of Hydrogen Sulphide on Sulphones. Influence of Solvents on Chemical Change. By R. OTTO (*J. pr. Chem.*, [2], 49, 378—391; compare *Abstr.*, 1893, i, 344).—Benzenesulphonic chloride is reduced by hydrogen sulphide in aqueous alcohol, with

greater difficulty in ether, particularly in absence of water; the reduction is still more difficult in methylic alcohol, benzene, or acetic acid.

The following are reducible by hydrogen sulphide in aqueous ether:—Paratoluenesulphonic chloride, α - and β -naphthalenesulphonic chloride, sulphobenzidemetabenzendisulphonic chloride, and sulphobenzidemetasulphonic chloride. In aqueous alcohol, parabromobenzenesulphonic chloride and sulphobenzidemetadisulphonic chloride are reducible. Paratoluenesulphonic chloride cannot be reduced in benzene.

Phenylic thiobenzenesulphonate is reduced in anhydrous methylic alcohol, and in aqueous alcohol, but not in benzene. Ethylic benzenesulphinate is reducible alone. Benzenesulphinic acid is reduced in aqueous alcohol, anhydrous methylic alcohol, and in water; β -naphthalenesulphinic acid is reduced in anhydrous methylic alcohol, and in chloroform, but with difficulty in benzene.

Monosulphones, ethylenediphenylsulphone, ethylic paratoluenesulphonate and ethylic benzenesulphonate cannot be reduced.

β -Naphthyl bisulphide melts at 139° , not 132° . A. G. B.

The Carboxybenzilehydrazones. By K. AUWERS and A. CLOS (*Ber.*, 27, 1133—1140).—If benzile (1 mol.) is digested on the water bath with parahydrazinebenzoic acid (1 mol.), *benzilemonohydrazoneparacarboxylic acid*, $\text{C}_6\text{H}_5\text{O} \cdot \text{CPh} \cdot \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, is formed; but with more of the latter (2 mols.), *benziledihydrazoneparadicarboxylic acid*, $\text{C}_2\text{Ph}_2(\text{N}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH})_2$, is obtained. These are both yellow crystalline substances, and melt respectively at 212° and above 320° , with decomposition. If benzile- α -monoxime is heated for 24 hours at 100° with parahydrazinebenzoic acid in absolute alcoholic solution, *benzileoximehydrazoneparacarboxylic acid*, $\text{NOH} \cdot \text{CPh} \cdot \text{CPh} \cdot \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, is formed, melting at 249 — 250° ; the β -oxime yields no such compound. (For similar indifferent behaviour of the β -oxime, compare *Abstr.*, 1893, i, 354.) The *monacetyl derivative* of this acid melts at 176° , the *ethylic salt* at 226° . When the acid is heated for 12 hours at 140° with absolute alcohol containing a little hydrochloric acid, *ethylic triphenylosotriazoneparacarboxylate*, melting at 99° , is obtained; the corresponding *acid*, $\text{CPh} \cdot \text{N} \cdot \text{CPh} \cdot \text{N} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, melts at 258° . The ethylic salt is more conveniently prepared by heating benzilemonohydrazoneparacarboxylic acid (5 parts) with hydroxylamine hydrochloride (1 part) and absolute alcohol (4 parts) for 16—20 hours at 100° . In both cases, some *diethylic benziledihydrazoneparacarboxylate* is formed at the same time; it melts at 229° . This substance can only be prepared from the corresponding acid with great difficulty; it is necessary to treat the acid with the theoretical quantity of sodium ethoxide in alcoholic solution, add a little water, and heat with ethylic iodide in a tube at 100° .

Some ortho-compounds were prepared in the same way as the above-mentioned para-derivatives. *Benzilemonohydrazonorthocarboxylic* and *benziledihydrazonorthodicarboxylic acids* are yellow,

crystalline substances, melting at 212° and above 320 respectively. *Benzileoximehydrazoneorthocarboxylic acid* is colourless, and melts at 226° . In connection with the preparation of these substances, it was noticed that benzile and orthohydrazinebenzoic acid, when heated together at 120° in absolute alcoholic solution, yield E. Fischer's orthohydrazinebenzoic anhydride, $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix}$. When benzileoximehydrazoneorthocarboxylic acid is warmed with acetic anhydride, a yellowish substance is formed, which has the formula, $C_6H_5N_2O_2$, and is possibly a monacetyl derivative of the above anhydride.

A series of corresponding meta-compounds can also be obtained, but their preparation is difficult and the yield small, owing to the formation of resinous products. C. F. B.

Action of Ethylic Oxalate on Dibenzyl Ketone. By L. CLAISEN (*Ber.*, 27, 1353—1354).—Dieckmann (this vol., i, 324) has shown that ethylic glutarate interacts with ethylic oxalate forming a derivative of diketopentamethylene. One of the author's students showed (Ewan, *Diss. München*, 1890), that *diphenyltriketopentamethylene* (oxalaldibenzyl ketone), $CO \begin{smallmatrix} \text{CHPh} \cdot \text{CO} \\ \text{CHPh} \cdot \text{CO} \end{smallmatrix}$, is formed by treating dibenzyl ketone with ethylic oxalate in presence of sodium ethoxide. This compound undergoes isomeric change when heated above its melting point; the product seems to be a hydroxylactone, but the experimental evidence as to the mechanism of the change is not yet complete. A. R. L.

Sulphonation in the Naphthalene Series. By O. DRESSSEL and R. KOTHE (*Ber.*, 27, 1193—1210).—The following researches, undertaken for technical purposes, show that the rule proposed by Armstrong and Wynne (*Proc.*, 1890, 130), according to which a sulphonic-group never enters the naphthalene molecule in the ortho-, peri-, or para-position to a similar group originally present, is liable to some exceptions.

Sulphonation of 2-naphthylamine-2'-sulphonic acid. This substance when sulphonated by means of fuming acid (25 per cent. SO_3) in the cold yields three sulphonic acids, the potassium salts of which separate from aqueous solution in the following order.

2-Naphthylamine-1 : 2'-disulphonic acid. The potassium salt,



crystallises extremely well, whilst the *hydrogen potassium* salt forms indistinct, slender needles. When its diazo-derivative is converted into the hydrazine, and the latter is oxidised with copper sulphate, and converted into the sodium salt, sodium naphthalene-1 : 2'-disulphonate is obtained.

2-Naphthylamine-4 : 2'-disulphonic acid forms a hydrogen sodium salt which crystallises with $1H_2O$, and a barium salt which is sparingly soluble in cold water and crystallises in crusts made up of

prisms. This acid has been previously prepared by Schultz, and others.

2-Naphthylamine-4':2'-disulphonic acid has been previously described by Armstrong and Wynne (*Proc.*, 1890, 11). The product of the sulphonation of 2-naphthylamine-2'-sulphonic acid consists of about 50 per cent. of the last named acid, together with about 25 per cent. of each of the other two.

Sulphonation of 2-Naphthylamine-3:2'-disulphonic acid. This acid, the preparation of which is the subject of a German patent (46,711), and of which the constitution has been determined by Armstrong and Wynne (*Proc.*, 1890, 127), forms a hydrogen sodium salt which requires 50 parts of cold water to dissolve it. The normal sodium salt is more readily soluble, whilst the hydrogen barium salt is very sparingly soluble indeed. When this acid is sulphonated at the temperature of the water bath, the sole product is 2-naphthylamine-1:3:2'-trisulphonic acid, but when this or the original disulphonic acid is heated at 130° with fuming sulphuric acid, a change occurs and two new trisulphonic acids accompanied by a tetrasulphonic acid are produced.

2-Naphthylamine-1:3:2'-trisulphonic acid forms a hydrogen sodium salt of the formula, $\text{NH}_2\text{C}_{10}\text{H}_4(\text{SO}_3\text{H})(\text{SO}_3\text{Na})_2 + 4\text{H}_2\text{O}$, which crystallises in colourless plates and is readily soluble in water. When the acidified solution of one of the salts of this acid is boiled, the sulphonic group in the position 1 is removed in the form of sulphuric acid, and the original naphthylaminedisulphonic acid is regenerated, a reaction which is common to all the sulphonic acids of 2-naphthol and 2-naphthylamine which contain a sulphonic group in the position 1. The constitution also follows from the fact that this trisulphonic acid can be obtained by heating 2-naphthol-1:3:2'-sulphonic acid with ammonia.

2-Naphthylamine-3:3':2'-trisulphonic acid, obtained by heating the foregoing acid with fuming sulphuric acid at 130°, is separated from the isomeric acid which accompanies it by means of its less soluble hydrogen sodium salt. It can be converted by means of the hydrazine reaction into naphthalene-2:3:3'-trisulphonic acid.

2-Naphthylamine-3:4':2'-trisulphonic acid, which accompanies the foregoing compound, forms a hydrogen sodium salt which is moderately soluble, yielding a solution which has a green fluorescence, whereas the solutions of the salts of all the sulphonic acids hitherto referred to have a blue fluorescence. It can be converted into naphthalene-1:3:2'-trisulphonic acid, and since this can only yield two β -amido-derivatives, one of which has been described above, the constitution of this acid is proved.

2-Naphthylamine-1:3:3':2'-tetrasulphonic acid forms a characteristic barium salt, which is only very sparingly soluble in boiling water. When an acid solution of one of the salts of this acid is boiled, the sulphonic group in position 1 is removed in the form of sulphuric acid, whilst alkaline solutions may be evaporated without any decomposition occurring.

The formation of 2-naphthylamine-3:3':2'-trisulphonic acid is the first well established exception to the Armstrong-Wynne rule, and

the formation of the two isomeric, trisulphonic acids from naphthylamine-1 : 3 : 2'-trisulphonic acid at 130° in the presence of sulphuric anhydride, is, moreover, a very important instance of molecular change among this class of compounds.

Sulphonation of 2-Naphthol-2'-sulphonic acid. When this acid is sulphonated by means of concentrated acid at 100° the 3 : 2'-disulphonic acid is formed without any isomeric, but accompanied by the 1 : 3 : 2'-trisulphonic acid. When chlorosulphonic acid is employed, however, the reaction proceeds differently, 2-naphthol-1 : 2'-disulphonic acid being formed in the cold. The *potassium* salt of this acid forms compact crystals, readily soluble in hot water. This acid does not yield azo-colouring matters, and can be converted into the corresponding naphthylamine compound, of known constitution, by heating with ammonia. When boiled with acids, the sulphonic group in the α -position is eliminated.

2-Naphthol-1 : 3 : 2'-trisulphonic acid is prepared by treating 2-naphthol-2'-sulphonic acid with fuming sulphuric acid at 80–90° for some hours. The *sodium* and *barium* salts are readily soluble and the acid does not yield azo-colouring matters. When boiled with acids, it is converted into the 3 : 2'-disulphonic acid.

2-Naphthol-1 : 3 : 3' : 2'-tetrasulphonic acid is the sole product formed by the further sulphonation of the foregoing acid at 130°. The *sodium* salt is readily soluble, the *barium* salt sparingly soluble in water. The acid does not yield azo-colouring matters, and when boiled with acids is converted into the 2 : 3 : 3'-trisulphonic acid. The latter forms a *sodium* salt which is characterised by its slight solubility in water. The acid readily yields azo-colouring matters and, when heated with ammonia, passes into the corresponding 2-naphthylamine-3 : 3' : 2'-trisulphonic acid which has been described above.

A. H.

Crystalline Form of β -Methylnaphthalene. By H. WICHELHAUS (*Ber.*, 27, 1247).—The preparation of this compound has been previously described (*Abstr.*, 1892, 492). When gently heated, it sublimes and forms large lustrous monoclinic plates $a : b : c = 1.3040 : 1 : ?$ $\beta = 76^\circ 44'$. The observed forms were OP and α P. There is complete cleavage parallel to the base.

J. B. T.

Dinitrochrysin. By G. DARIER (*Ber.*, 27, 1045).—The nitrochrysin obtained by Piccard and quoted by the author (this vol., i, 207) as mononitrochrysin, is actually the dinitro-compound, identical with that described by the author.

A. H.

The Crystalline Constituents of Coto Bark. By O. HESSE (*Ber.*, 27, 1182–1186).—Re-examining his old specimens of cotoïn and cotoïu acetate, the author confirms the formulæ $C_{14}H_{11}O_4$ and $C_{14}H_{10}O_4Ac_2$, put forward by Ciamician and Silber (this vol., i, 255). He has also confirmed this molecular weight by Raoult's freezing-point method. The author believes that the methoxyhydroxyphenylcoumarin acetate obtained by Ciamician and Silber when acetylising cotoïn was due to impurity of their material, as he obtained no such compound. Cotoïn appears to be dimorphous, crystallising in prisms and plates, both of which yield the same acetate.

The substance previously described by the author and Jobst as dicotoïn appears not to be a single substance. When acetylated, it yields cotoïn acetate. When fused with potash, it yields benzoic acid, the methoxyhydroxyphenylcoumarin of Ciamician and Silber (*loc. cit.*), and a substance to which the author ascribes the name oxymethylphenylcoumarin and the formula $O < \begin{smallmatrix} \text{C} \cdot \text{Ph} - \text{CO} \\ \text{CH} \cdot \text{C}_6\text{H}_4\text{Me} \end{smallmatrix} > \text{O}$. This sub-

stance crystallises in long, white needles, melts at 221° , and is soluble in alcohol. It does not yield an acetate with acetic anhydrides, neither does hydriodic acid eliminate methyl iodide. The compound, therefore, does not contain either a hydroxy- or methoxy-group. An analogous oxyphenylcoumarin melting at 61° , and giving no coloration with an alcoholic solution of ferric chloride, was also obtained from dicotoïn, by treating it with light petroleum.

How these compounds exist in the dicotoïn, whether free or combined, remains undetermined. L. T. T.

The Pyridine Series. By W. MARCKWALD (*Ber.*, **27**, 1317—1339).

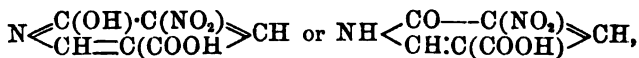
—The formation of 2:5 amidonicotinic acid from the corresponding chloronicotinic acid and ammonia has already been described (*Abstr.*, 1893, i, 727). Several derivatives of the amido acid, with both positive and negative radicles, are now described, among them the *picrate*, which melts at 248° .

2-Amidopyridine (*loc. cit.*) forms a *platinochloride*, melting at 231° , a *picrate* melting at 216 — 217° , and a *benzoyl* derivative, $\text{C}_6\text{NH}_4\text{NHBz}$, melting at 165° ; the latter yields a *picrate* melting at 146° . *Pyridylphenylthiocarbamide*, $\text{C}_6\text{NH}_4\text{NH} \cdot \text{CS} \cdot \text{NHPh}$, can only be obtained by boiling 2-amidopyridine with alcohol and phenylthiocarbimide; it forms white, lance-shaped crystals, and melts at 168° . 2-Amidopyridine remains unaltered when sodium nitrite is added to its solution in dilute hydrochloric acid; if, however, a strong solution of sodium nitrite is added to its solution in concentrated hydrochloric acid, 2-chloropyridine is formed. Nitrous acid does not react with 2:3-amidonicotinic acid in presence even of concentrated hydrochloric acid, but it is diazotised when its solution in concentrated sulphuric acid is treated with pulverised sodium nitrite in the cold.

Amidolutidinedicarboxylic acid, $\text{N} < \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{COOH}) \\ \text{CMe} \cdot \text{C}(\text{COOH}) \end{smallmatrix} > \text{C} \cdot \text{NH}_2$, is obtained by treating chlorolutidinedicarboxylic acid (Conrad and Epstein, *Abstr.*, 1887, 501) with ammonia at 130° ; it crystallises from hot water in long, white needles, forms derivatives with both positive and negative radicles, and melts at 263° with evolution of carbonic anhydride, 4-amidolutidine being produced. The latter melts at 186° , and boils at 246° ; the *picrate* melts at 194 — 195° , and the *platinochloride* decomposes at 250° . The *acetyl*-derivative, $\text{C}_7\text{NH}_5\text{NHAc}$, crystallises from water in long, monohydrated needles melting at 78° ; the *anhydrous* compound melts at 113° , forms a *platinochloride* melting at 235° , and a *picrate* melting at 97 — 98° . 4-Amidolutidine yields Conrad and Epstein's chlorolutidine (*loc. cit.*), when it is dissolved in concentrated hydrochloric acid and treated with sodium nitrite; when diazotised in presence of concentrated sulphuric acid, however, if the

resulting liquid be diluted by the addition of ice, lutidone sulphate is formed, whilst, if it be poured into absolute alcohol, *ethoxylutidine*, $N \langle \begin{smallmatrix} CMe \cdot CH \\ CMe \cdot CH \end{smallmatrix} \rangle C \cdot OEt$, is obtained. This is a colourless, transparent liquid boiling at 207° ; the *platinochloride* melts and decomposes at 204° , and the *picrate* melts at 112° . 4-Amidolutidine remains unaltered when treated with tin and hydrochloric acid, but may be reduced by sodium and alcohol, giving rise to 2 : 5 lupetidine (Ladenburg, *Annalen*, **247**, 87), the *thiocarbamate* of which melts at 108° , and *amidolupetidine*, $NH \langle \begin{smallmatrix} CHMe \cdot CH_2 \\ CHMe \cdot CH_2 \end{smallmatrix} \rangle CH \cdot NH_2$, which boils at $195-196^\circ$. Ethoxylutidine yields lupetidine on reduction with sodium and alcohol. *Bromamidolutidine*, $N \langle \begin{smallmatrix} CMe \cdot CH \\ CMe \cdot CBr \end{smallmatrix} \rangle C \cdot NH_2$, is obtained by adding the calculated quantity of bromine to a solution of 4-amidolutidine in hydrochloric acid; it crystallises from water in monohydrated felted needles, melting at 89° ; the *anhydrous* compound melts at 129° , and distils without decomposition. The *platinochloride* melts at 220° , and the *picrate* melts at $197-198^\circ$. *Dibromamidolutidine*, $N \langle \begin{smallmatrix} CMe \cdot CBr \\ CMe \cdot CBr \end{smallmatrix} \rangle C \cdot NH_2$, forms white needles, melts at 152° , and can only be diazotised when dissolved in concentrated sulphuric acid, under which circumstances dibromolutidine is produced. *Dibromolutidine platinochloride* melts at 270° , and the *picrate* melts at 255° .

Nitramidonicotinic acid (Abstr., 1893, i, 727) is prepared by adding amidonicotinic acid nitrate to concentrated sulphuric acid, and gradually raising the temperature to 100° ; when diazotised in presence of concentrated sulphuric acid, it yields *nitrohydrozynecotinic acid*,



which forms feathery crystals, and melts with decomposition at 250° .

Diamidonicotinic acid, $N \langle \begin{smallmatrix} C(NH_2) \cdot C(NH_2) \\ CH = C(COOH) \end{smallmatrix} \rangle CH$, is obtained by reducing the nitro-compound, preferably with tin and hydrochloric acid; it forms a grey powder containing $1H_2O$, which is expelled at 120° , and does not melt at 300° ; its basic properties are more pronounced than its acidic; the *picrate* melts at 245° .

Azimidonicotinic acid, $COOH \cdot C \langle \begin{smallmatrix} CH - C - N \\ CH \cdot N \cdot C \cdot NH \end{smallmatrix} \rangle N$, is obtained by treating the last-mentioned diamido-derivative with nitrous acid; it separates from water in white, felted crystals, containing $1H_2O$, and decomposes at about 270° .
A. R. L.

3-Chloroquinoline. By A. CLAUS and A. SCHEDLER (*J. pr. Chem.*, [2], **49**, 355-378).—3-Chloroquinoline melts at $40-41^\circ$, and boils at $261-262^\circ$ (740 mm.). The *perbromide* of its hydrobromide, $C_9NH_4Cl \cdot HBr \cdot Br_2$, crystallises in yellow needles, and melts and decomposes at 129° . When heated at $180-190^\circ$, the *perbromide* yields the hydrobromide of 4'-bromo-4-chloroquinoline; the free base crystal-

lises in small, colourless needles, melts at 112° , and is volatile with steam; the *hydrochloride* (m. p. 168°), *platinochloride* and *methiodide* (m. p. $286-287^{\circ}$) are described.

4-Nitro-3-chloroquinoline crystallises in colourless prisms, melts at 129° , and sublimes when heated; the *hydrochloride* melts and decomposes at 215° ; the *platinochloride* does not melt at 320° ; the *nitrate* melts and decomposes at 194° ; the *methiodide* melts at 243° . The *methochloride* melts and decomposes at 178° ; its *platinochloride* is described. The *sulphate* melts at $227-228^{\circ}$.

4-Amido-3-chloroquinoline crystallises (with $1\text{H}_2\text{O}$) in long, silky, yellow needles; the crystals melt at $115-119^{\circ}$, and the anhydrous compound melts at $132-136^{\circ}$. The *hydrochloride* crystallises in blood-red tables, melts at $215-220^{\circ}$, and dissolves in water and alcohol; the *platinochloride* melts and decomposes at 250° .

4:3-Dichloroquinoline, prepared from the amido-derivative through the diazo reaction, crystallises in colourless needles, melts at 85° , and dissolves in alcohol and in light petroleum, but only sparingly in hot water; the *platinochloride* is described.

4-Hydroxy-3-chloroquinoline is obtained when the 4-diazo-3-chloroquinoline sulphate is treated with dilute cuprous chloride solution; it crystallises in vitreous needles, melts at $183-184^{\circ}$, and dissolves in most solvents; the *platinochloride* and the *methiodide* (m. p. $199-201^{\circ}$) were obtained.

1-Nitro-3-chloroquinoline is a bye-product in the nitration of quinoline in sulphuric acid, but the sole product when nitric acid is used alone; it crystallises in slender, colourless needles, melts at 158° , sublimes, and dissolves in alcohol and in hot water; the latter solvent separates it from the 4-nitro-derivative. The *platinochloride* decomposes at 251° .

1-Amido-3-chloroquinoline crystallises in colourless needles, melts at 73° , and sublimes. It forms two *hydrochlorides*; $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{NH}_2\cdot\text{Cl}\cdot 2\text{HCl}$ forms large, red crystals, melts at 228° , and is decomposed by water into $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{NH}_2\cdot\text{Cl}\cdot\text{HCl}$, which forms small, yellow crystals, and melts at 208° . The *platinochloride* of the latter salt is described. The *methiodide* of this amidochloroquinoline crystallises in orange-yellow needles, and melts at 178° .

3-Chloroquinoline-4-sulphonic acid crystallises, with $1\text{H}_2\text{O}$, in tables; its *potassium* salt, with $1\frac{1}{2}\text{H}_2\text{O}$, is described.

3-Chloroquinoline-1-sulphonic acid crystallises in colourless, vitreous needles; its *potassium* salt is described. A. G. B.

Reduction and Condensation of Thiazoles. By A. SCHUFTAN (*Ber.*, 27, 1009-1012).—According to Schatzmann (*Annalen*, 261, 6), dimethylthiazole is converted, by reduction with sodium and alcohol, into ethylamine and propyl mercaptan. When, however, the reduction is effected by adding the heated solution of the thiazole in alcohol to the sodium, *ethylisopropylamine*, $\text{NH}\cdot\text{Et}\cdot\text{Pr}^i$, and hydrogen sulphide are formed. The new base is a colourless liquid, which is miscible with water and alcohol, and boils at 76° . The *platinochloride* crystallises in reddish-yellow needles melting at 180° . Nitrous acid converts the base into *ethylisopropyl nitrosamine*, which is a

yellow oil boiling at 70° (11 mm.). *Ethylisopropylphenylthiocarbamide*, $\text{NEtPr}^s\text{SC}\cdot\text{NHPh}$, forms long, white, very refractive needles, and melts at 132°.

When dimethylthiazole is heated at 160° with formaldehyde solution, *dimethylthiazolylalkine*, $\begin{array}{c} \text{S}-\text{CH} \\ | \\ \text{CMe:N} \end{array} > \text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, is formed.

This compound is an oily, faintly alkaline liquid. The *platinochloride* melts and decomposes at 169°; the *hydrochloride* crystallises in fan-shaped groups of long, colourless needles, and the *aurochloride* melts at 136°. A. H.

Pyrazines. By C. STOEHR (*J. pr. Chem.*, [2], 49, 392—403).—This paper constitutes a rejoinder to Wolff (*Abstr.*, 1893, i, 729).

Methylpyrazine, $\text{C}_4\text{H}_5\text{MeN}_2$, is a limpid, strongly refractive, colourless liquid; it remains liquid at 0°, boils at 136—137°, and has a specific gravity of 1.0441 at 0°/4°.

Pyrazine picrate melts at 156°. Pyrazine methiodide crystallises in yellow laminæ, and is insoluble in ether and benzene, but soluble in alcohol. A. G. B.

Constitution of Phenylpyrazolone. By S. RUHEMANN and R. S. MORRELL (*Ber.*, 27, 1090—1091).—In connection with the recent work of Stolz (this vol., i, 259) and v. Rothenburg (this vol., i, 350), the authors show that the phenylpyrazolone melting at 118° prepared by them (*Trans.*, 1892, 791) can only be 1-phenyl-3 or 5-pyrazolone. W. J. P.

Cyanacetophenone and Hydroxylamine. By R. v. ROTHEMBURG (*Ber.*, 27, 1095—1096).—The compound obtained by the interaction of these substances, and described by Obregia (*Abstr.*, 1892, 324), has not the properties of a pyrazolone derivative. It is, therefore, not 3-phenylpyrazolone, as Obregia supposed, but is probably

3-phenyl-5-imido-oxazoline, $\begin{array}{c} \text{C Ph}\cdot\text{CH}_2 \\ | \\ \text{N} \end{array} \text{—} \text{O} > \text{C}\cdot\text{NH}$, or else the tautomeric 3-phenyl-5-amido-oxazole, $\begin{array}{c} \text{C Ph}\cdot\text{CH} \\ | \\ \text{N} \end{array} \text{—} \text{O} > \text{C}\cdot\text{NH}_2$. C. F. B.

3 : 5-Dimethylpyrazole. By R. v. ROTHENBURG (*Ber.*, 27, 1097—1098; compare Marchetti, *Abstr.*, 1893, i, 179 and 674, and Buchner and Papendieck, *ibid.*, 432).—Hydrazine hydrate and ethylacetone yield 3 : 5-dimethylpyrazole, $\begin{array}{c} \text{N}=\text{CMe} \\ | \\ \text{NH}\cdot\text{CMe} \end{array} > \text{CH}$, which melts at 105—108°, and boils at about 220°; its *platinochloride*,



decomposes at about 180°. When oxidised with the theoretical amount of alkaline permanganate, it yields Marchetti's 5-methylpyrazole-3-carboxylic acid, $\begin{array}{c} \text{N}:\text{C}(\text{COOH}) \\ | \\ \text{NH}\text{—}\text{CMe} \end{array} > \text{CH}$. If double the above

quantity of permanganate is used, 3 : 5-pyrazoledicarboxylic acid is formed, already described by Marchetti and by Buchner.

C. F. B.

Pyrazolone from β -Aldoximeacetic acid. By R. v. ROTHENBURG (*Ber.*, 27, 1098—1099).—Pechmann's β -aldoximeacetic acid (β -oximidopropionic acid), $\text{NOH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$ (*Abstr.*, 1891, 1458), was first prepared in solution by warming together coumalinic acid, hydroxylamine hydrochloride, and soda; and to the mixture, neutralised with hydrochloric acid, the calculated quantity of hydrazine hydrate was added, and the whole allowed to remain at 50—60°. The hydroxylamine salt of the pyrazolone thus formed can be separated into its constituents by adding sodium carbonate, and distilling over the pyrazolone with steam.

C. F. B.

Isomeric *n*-Phenylpyrazolones. By R. v. ROTHENBURG (*Ber.*, 27, 1099—1100).—The compound erroneously described (*Ber.*, 27, 946) as 2-phenylisopyrazolone-3-carboxylic acid is really 2-phenylisopyrazolone-4-carboxylic acid, $\text{N}^{\text{Ph}}\cdot\text{CH} \begin{array}{l} \text{NH} \\ \text{NH} \end{array} \text{—CO} > \text{C}\cdot\text{COOH}$.

C. F. B.

Octohydro-1:8-naphthyridine and 2 ω -Amidopropylpiperidone. By A. REISSERT (*Ber.*, 27, 979—984; compare *Abstr.*, 1893, i, 687).—When di- γ -amidodipropylacetic acid, containing a certain amount of carbonate, formed by absorption of atmospheric carbonic anhydride, is submitted to dry distillation, octohydronaphthyridine passes over, whilst a residue consisting of the carbonate of 2 ω -amidopropylpiperidone, $\text{CH}_2 < \begin{array}{l} \text{CH}_2\cdot\text{CH}_2 \\ \text{NH} \end{array} \text{—CO} > \text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, is left. By the action of strong soda on this salt, the free base is obtained as a colourless, odourless, strongly basic oil, which is tolerably soluble in water; it gives the carbylamine reaction, and cannot be distilled, since, when heated, it decomposes into water and octohydronaphthyridine. The *hydrochloride*, $\text{C}_8\text{H}_{10}\text{N}_2\text{O}\cdot\text{HCl}$, melts at 159.5°, and the *platinochloride* at 220°. The *picrate* forms soft, yellow needles melting at 207°. Benzoic chloride converts the base into a *monobenzoyl derivative*, $\text{C}_8\text{H}_{10}\text{N}_2\text{O}\cdot\text{COPh}$, which melts at 151°.

Octohydronaphthyridine, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\text{—N}\cdot\text{C}\cdot\text{NH—CH}_2 \end{array}$, forms white needles, melts at about 67°, and boils at 248°. It combines very readily with the atmospheric carbonic anhydride, forming the *carbonate*, which is readily soluble in water, and melts at 156°. The free base is readily soluble in water, and moderately so in alcohol, forming strongly alkaline solutions; it has a characteristic alkaloidal odour. The *hydrochloride* could only be obtained as a syrup; the *picrate* melts at 208—209°.

n-Methyloctohydronaphthyridine is prepared by the direct action of methylic iodide on the base or its carbonate. It is a basic oil, and yields a *picrate*, which melts at 209°.

A. H.

Action of Hydrazine on Imido-Ethers. By A. PINNER (*Ber.*, 27, 984—1009; compare *Abstr.*, 1893, i, 710).—When benzimido-

ether and hydrazine are brought together, *benzenylhydrazidine*, $\text{NH}_2\cdot\text{NH}\cdot\text{CPh}\cdot\text{NH}$, is the first product, and this immediately reacts with hydrazine or benzimido-ether to produce secondary compounds. The free base cannot be obtained pure, but the *picrate*,



may be prepared by treating benzimido-ether hydrochloride with hydrazine sulphate dissolved in aqueous potash, filtering off the dibenzenylhydrazidine which separates, acidifying, and, after some days, adding picric acid. It forms short, thick, yellow prisms, and is soluble in alcohol and hot water.

Benzoylbenzenylhydrazidine, $\text{COPh}\cdot\text{NH}\cdot\text{NH}\cdot\text{CPh}\cdot\text{NH}$, may be obtained by shaking the alkaline filtrate mentioned above with benzoic chloride. It crystallises in long, lustrous prisms, and melts, after losing the elements of water, at 188° . This substance is identical with the compound formerly described (*loc. cit.*) as melting at 170° . It is a strong base and reduces copper solution on boiling. The *aurochloride* crystallises in yellow prisms and melts at 197° . When it is heated to 120° , it is converted into diphenyltriazole.

Benzenylhydrazidine is converted by the action of nitrous acid into phenyltetrazotic acid, identical with that described by Lössen (*Annalen*, 263, 101). It also reacts with glyoxal to form *glyoxalene-dibenzenylhydrazidine*, $\text{C}_2\text{H}_2(\text{N}\cdot\text{NH}\cdot\text{CPh}\cdot\text{NH})_2$, which crystallises in short, slender, lustrous, yellow needles, is only slightly soluble in the usual solvents, and melts and decomposes at 220° , after softening at 210° .

Dibenzenylhydrazidine, $\text{N}_2\text{H}_2(\text{CPh}\cdot\text{NH})_2$, has been previously described. It appears in many reactions to behave as a diamido-compound of the formula $\text{NH}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}_2$. It is a strong diacid base, and is very unstable in acid solution although stable in alkaline liquids. The hydrochloride, $\text{C}_{14}\text{H}_{14}\text{N}_4\cdot 2\text{HCl}$, sublimes, when heated, without melting. The *nitrate* forms white, sparingly soluble prisms, and melts at 114° , whilst the *picrate* melts at about 220° . *Diacetyldibenzenylhydrazidine* forms white needles melting at 98° , and is readily soluble in alcohol.

When dibenzenylhydrazidine is allowed to remain in acid solution for some time, or when it is treated with zinc dust and acetic acid, it is converted into *diphenyltriazole*, $\text{CPh}\langle\overset{\text{N}}{\text{NH}\cdot\text{N}}\rangle\text{CPh}$; this crystallises with $1\text{H}_2\text{O}$ in white prisms which effloresce at 100° ; it is insoluble in water and in dilute acids, moderately soluble in alcohol, melts at 188° , and boils and decomposes at about 280° . *Acetyldiphenyltriazole* melts at 105° .

The action of nitrous acid on dibenzenylhydrazidine is of a complex character, and varies with the conditions of the experiment. When a large excess of sodium nitrite and acetic acid is used, phenyltetrazotic acid and dibenzamide are the main products, the latter being probably formed from bezonitrile, the primary reaction being as follows: $\text{C}_{14}\text{H}_{14}\text{N}_4 + \text{HNO}_2 = \text{C}_7\text{H}_5\text{N}_3 + \text{C}_7\text{H}_5\text{N} + 2\text{H}_2\text{O}$. When 2 mols. of sodium nitrite and hydrochloric acid are employed, a crystalline precipitate is formed, consisting of the *hydrochloride of benzoyl-*

benzenylhydrazidine, $C_{14}H_{13}N_3O \cdot 2HCl$, which melts at 92° , solidifies when further heated, and finally melts at 172° . It is remarkable that benzenylhydrazidine is a monacid base, whilst the benzoyl-derivative combines with 2 molecules of an acid. In this reaction, dibenzenylhydrazidine reacts as though it contained two amido-groups.

When 4 mols. of sodium nitrite are used, and the mixture is allowed to remain over night, a mass of white crystals is obtained. These are readily soluble in alcohol, slightly in benzene, and melt and deflagrate at 110° . The compound shows Liebermann's reaction, and has the formula $OH \cdot CPh \cdot N \cdot N \cdot CPh \cdot NH \cdot NO, HCl + H_2O$. When it is heated with water, benzoylbenzenylhydrazine is formed.

If the same mixture, containing 4 mols. of sodium nitrite, be allowed to remain for 4—8 days, the crystalline mass partially dissolves, benzoylbenzenylhydrazidine and dibenzenylisazoxime, $CPh \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ N \cdot N \end{smallmatrix} CPh$, being formed. In all these reactions, a small amount of phenyltetrazotic acid is also produced.

Diphenyldihydrotetrazine, $CPh \begin{smallmatrix} NH \cdot NH \\ \diagup \quad \diagdown \\ N \quad N \end{smallmatrix} CPh$, is the chief product of the action between 2 mols. of benzimido-ether and 3 mols. of hydrazine sulphate. It does not appear to be formed from dibenzenylhydrazidine by the action of hydrazine, and is probably, therefore, derived from the monobenzenylhydrazidine in the presence of hydrazine. It unites with methylic iodide to form the *double compound*, $C_{14}H_{12}N_4 \cdot MeI$, which melts and decomposes at 128° .

When diphenyldihydrotetrazine is heated with acetic acid and zinc dust, or alcohol and sodium, diphenyltriazole is formed; if, on the other hand, it is boiled with hydrochloric acid of 25 per cent., it is converted into the isomeric *diphenylisodihydrotetrazine*, $CPh \begin{smallmatrix} N \cdot NH \\ \diagup \quad \diagdown \\ NH \cdot N \end{smallmatrix} CPh$. This compound was described in the previous paper under the name of benzenylimidonitrile as having half the molecular weight which is now ascribed to it. The *aurochloride* melts at 215° . *Monacetyldiphenylisodihydrotetrazine* melts at 267° and forms small white prisms. The *diacetyl*-derivative forms compact, white prisms, which melt at 215° . The *diacetyl*-derivative obtained from diphenyldihydrotetrazine was found to have the constitution which had previously been ascribed to it.

Diphenylisodihydrotetrazine is converted by nitrous acid into diphenyltriazole; like its isomeride, this combines with 1 mol. of methylic iodide to form a substance, which crystallises in compact prisms and melts and decomposes at 150° . *Dibenzenylisazoxime* or *diphenylbi-azoxole*, $CPh \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ N \cdot N \end{smallmatrix} CPh$, has already been mentioned as being formed by the action of nitrous acid on benzoylbenzenylhydrazidine and dibenzenylhydrazidine. From hot alcohol, to which a little potash has been added, it crystallises in large iridescent plates of the anhydrous substance, whilst, by the evaporation of the cold solution, slender needles are obtained, which contain $1H_2O$. The hydrated crystals melt at 80° , the anhydrous at 140° , and the compound distils, without decomposing, above 360° . The isazoxime combines with

silver nitrate to form long, silky needles, which are acted on by light and melt and decompose at 275° .

Although diphenyldihydropyridazine is scarcely affected by aqueous soda, its oxidation product, diphenylpyridazine, is converted by the action of alcoholic potash into a compound of the constitution CHPh:N:N:CPh:OH , which crystallises in lustrous, colourless prisms, melts at 206° , and is slightly soluble in alkalis, insoluble in acids.

Dibenzimidine, $\text{C}_{14}\text{H}_{13}\text{N}_3$, which is also found among the products of the reaction between benzimido-ether and hydrazine, is probably formed from the benzenylhydrazidine. It yields a *triacetyl*-derivative, which melts at 94° , and an *aurochloride*, which melts at 145° . It is soluble in concentrated hydrochloric acid and in strong aqueous alkalis.

A. H.

Coniine and its Compounds. By J. SCHORM (*Zeit. angew. Chem.*, 1894, 266—267).—In extracting coniine from hemlock seeds, the author recommends, as an improvement on his previously described method (*Abstr.*, 1882, 215), that the crude solution of chlorides should be evaporated to dryness and the residue heated on the sand bath until the resinous impurities are destroyed and the residue has become odourless. It is then dissolved and filtered, and if the filtrate is coloured, should be treated with animal charcoal, or, better, with hydrogen peroxide, until colourless, and the solution evaporated to a small bulk; coniine hydrobromide crystallises out whilst the mother liquor contains conhydrine and a new base. To obtain these, the solution is rendered alkaline and the bases extracted with ether, from which extract the conhydrine crystallises out, leaving the new base (which is under investigation) as an oil.

The hydrated coniine (in the form in which it separates from the steam distillate) has a sp. gr. of 0.900 at 12° , and at 100° gives up 20 per cent. of water, passing into the anhydrous base. It is the best form in which to keep the base. The author has prepared many of the salts from the pure base.

The author recommends the use of hydrogen peroxide for purifying natural alkaloids, but it must only be used in neutral solutions of the chlorides, or it is liable to cause loss of the alkaloid.

L. T. T.

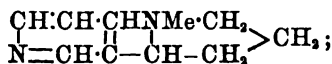
Nicotine (Metanicotine). By A. PINNER (*Ber.*, 27, 1053—1061).—The substance prepared by Étard (*Abstr.*, 1893, i, 736) and considered by him to be benzoynicotine, is really a benzoyl-derivative of a secondary base isomeric with nicotine, which the author terms metanicotine. The derivative is hence benzoylmetanicotine.

Benzoylmetanicotine picrate, $\text{C}_{10}\text{H}_{13}\text{N}_2\cdot\text{OBz}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, crystallises in thin, flattened prisms melting at 128° , and is soluble in alcohol; it is advantageously employed in place of the platinochloride in the purification of the base.

Metanicotine, $\text{C}_{10}\text{H}_{13}\text{N}_2$, is prepared by heating its benzoyl-derivative with concentrated hydrochloric acid in a closed tube at 100° ; it boils at 275 — 278° , has a feeble odour recalling that of nicotine, is optically inactive, and has more pronounced basic properties than nicotine. It

is sparingly soluble in ether. A benzoyl-derivative, identical with that prepared from nicotine, is obtained on adding benzoic chloride to its solution in soda. The *hydrochloride*, $C_{10}H_{14}N_2 \cdot 2HCl$, forms a colourless, hygroscopic, crystalline mass, and is readily soluble in water or alcohol. The *platinochloride* crystallises in beautiful, yellow prisms, decomposing with partial fusion at about 255° . The *aurochloride* forms yellow prisms melting at 160° on rapid heating, whilst *nicotine aurochloride* is obtained as a scarcely crystalline precipitate, decomposing with partial fusion at above 180° . *Metanicotine picrate*, $C_{10}H_{14}N_2 \cdot 2C_6H_3N_3O_7 \cdot H_2O$, is obtained in thin, crystalline threads, melting first at 114° , then solidifying and again melting at 163° .

The author again (Abstr., 1893, i, 736) criticises adversely the constitutional formula attributed by Etard to nicotine; the base is probably a methyl- β -pyridylpyrrolidine, having the constitution



metanicotine would then probably be methyl- β -pyridyl- δ -butylenamine, $\text{CH} < \begin{array}{c} \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{N} = \text{CH} \end{array} > \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHMe}$. W. J. P.

Hydrastine. By E. SCHMIDT (*Arch. Pharm.*, **231**, 541—579; compare Abstr., 1890, 533, 1168; 1893, i, 116).—The author describes the decomposition of hydrastonic acid, and strengthens the evidence in favour of the constitutional formula for hydrastine advocated by Freund (*Annalen*, **271**, 345), supporting his conclusions by a further study of the methyl derivatives of the alkaloid.

Hydrastonic acid is the non-nitrogenous substance melting at 169° , obtained by decomposing methylhydrastine methiodide with aqueous potash (Abstr., 1890, 533 and 1168). Analysis of the free acid and of its silver salt establishes its monobasic character, and confirms the composition, $C_{20}H_{18}O_7$, already ascribed to it. Hydrastonic acid contains two methoxyl groups, and, whilst not attacked by acetic chloride, unites readily with hydroxylamine to form an *oxime*, $C_{20}H_{18}O_6 \cdot \text{NOH}$; the addition of 2 atoms of bromine affords evidence of the unsaturated character of the acid. Oxidation in neutral solution with potassium permanganate gives rise to hemipinic acid, together with an acid of unknown constitution, which melts at 234° . If, however, an alkaline solution is employed, *hydrastolactone*, $C_{10}H_8O_6$, is formed; this crystallises in long needles, and melts at 154° . It resembles in its properties cotarnelactone (Abstr., 1890, 528), the intermediate product in the oxidation of cotarone to cotarnic acid. The *benzoyl*- and *acetyl*-derivatives are well defined, the latter forming thick rectangular plates which melt at 115° . In addition to hydrastolactone, the oxidation of hydrastonic acid leads to the formation of hemipinic, hydrastic, and oxalic acids, together with a small quantity of an unknown monobasic acid, isomeric with hemipinic acid, but differing from it in character, for whilst the latter substance melts at 162° the new acid fuses with evolution of gas at 146 — 148° , resolidifies at 167° , and finally melts at 220° . The resemblance shown by hydrastolactone to cotarnelactone is borne out by its behaviour on further

By boiling an alcoholic solution of hydrastine methiodide with a large excess of strong aqueous ammonia, methylhydrastamide has been obtained (Abstr., 1891, 92). If, however, the dry methiodide is heated for two hours with alcoholic ammonia at 100° under pressure, it yields *methylhydrastimide hydriodide*, $C_{22}H_{21}N_2O_2, HI$, which crystallises from alcohol in yellow needles melting at 233° .

Hydrastinine, the product of the oxidation of hydrastine with dilute nitric acid (Abstr., 1887, 383), is obtained in small quantities when a mixture of hydrastine with 10 parts of soda-lime is submitted to dry distillation in an atmosphere of hydrogen. M. O. F.

New Compounds of Cinchona Alkaloids with Ethylic Iodide. By Z. H. SKRAUP and F. K. v. NORWALL (*Montsch.*, 15, 37—52).—In this paper, particulars are given of work which has been previously published in outline (compare Abstr., 1893, i, 738). In order to distinguish between the isomeric compounds of an alkaloid with ethylic iodide, the authors suggest that one compound should be represented by the name of the alkaloid preceded by the term "iodoethyl," whilst the second should be represented by a name in which that of the alkaloid is followed by the term "ethiodide." For example, they propose to call the colourless product obtained from free cinchonine and ethylic iodide, "iodoethylcinchonine," whilst the yellow substance prepared from cinchonine hydriodide and ethylic iodide would be named "cinchonine ethiodide."

The following compounds are described:—*Cinchonine ethiodide hydriodide*, $EtI, C_{19}H_{23}N_2O, HI$, crystallises in yellow prisms, commences to decompose, with evolution of iodine, at 200° , melts with decomposition at 245 — 250° , and when treated with ammonia yields *cinchonine ethiodide*. The latter crystallises from water in orange-yellow needles, blackens at 170° , and slowly melts at about 184° . *Iodoethylcinchonine hydriodide*, the isomeride, crystallises in pale yellow prisms, having the composition $EtI, C_{19}H_{23}N_2O, HI + H_2O$, melts at 220 — 222° , and is formed when a solution of iodoethylcinchonine (m. p. 259 — 260°) in hydrochloric acid is treated with potassium iodide. *Cinchonidine ethiodide hydriodide*, which crystallises in yellow prisms and melts at 243° , yields, when treated with ammonia, *cinchonidine ethiodide*, which forms small, yellow needles, and melts with decomposition at 175° . *Iodoethylcinchonidine hydriodide*, $EtI, C_{19}H_{23}N_2O, + H_2O$, crystallises in light yellow needles, is orange-yellow at 100 — 130° , loses iodine at 140 — 150° , and melts with decomposition at 231° .

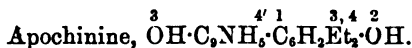
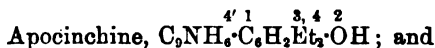
Quinine ethiodide hydriodide, $HI, C_{20}H_{24}N_2O_2, EtI + 3H_2O$, crystallises from water in brownish-yellow scales, which melt at 75 — 80° , and from alcohol in deep yellow crystals, melting at 234° . Treated with sodium hydroxide or with ammonia, it forms *quinine ethiodide*, $C_{20}H_{24}N_2O_2, EtI + 3H_2O$. This crystallises from alcohol in long needles, softens at 85° , melts at 93° , and unites with ethylic iodide to form *quinine diethiodide* (m. p. 140°). *Iodoethylquinine hydriodide* melts at 200° , and crystallises in needles or small grains.

Quinidine diethiodide, $C_{20}H_{24}N_2O_2, 2EtI + 3H_2O$, prepared from

colourless iodoethylquinidine and ethylic iodide at 100°, crystallises in bright yellow prisms and melts at 134°. G. T. M.

The Hydrolytic Decomposition of Chinine and Cinchine. By W. KOENIGS (*Ber.*, 27, 900—907).—It has been shown that chinine and cinchine, when boiled with concentrated hydrogen bromide, are converted into derivatives of γ -phenylquinoline, namely, apochinine and apocinchine. If, however, cinchine and chinine are heated with phosphoric acid at 170—180°, they are decomposed, yielding lepidine and paramethoxylepidine respectively, and also a new compound, $C_9H_{15}NO_2$, which the author names merochinine.

For reasons which are given below, the author assigns the following constitutions to apocinchine and apochinine, namely,



The author has already shown (*Abstr.*, 1893, i, 376) that the ethyl ether of apocinchine, on oxidation, yields ethylapocinchenic acid, a lactone, and finally quinolinephenetoildicarboxylic acid containing the two carboxyl groups in the ortho-position relatively to one another. The orthohydroxy- γ -phenylquinoline, prepared from orthomethoxybenzoylacetone, is found to be identical with the hydroxyphenylquinoline obtained from apocinchine.

Apocinchine, when treated with sodium nitrite in acetic acid solution, yields a *mononitro-derivative*, melting at 228°, and this, on reduction, is converted into *amilo-apocinchine*, melting at 220°. The latter, on oxidation, yields cinchoninic acid, and when dissolved in sulphuric acid and treated with lead peroxide, gives a dark red coloration, which is probably due to the formation of a quinone or quinhydrone.

When apochinine is heated with zinc chloride, ammonia, and ammonium chloride at 240—250°, it is converted into 4-amidoapocinchine, which melts at 226—228°, and this is converted through the diazo-compound into apocinchine.

Merochinine, $C_9H_{15}NO_2$, crystallises in colourless needles, melts at 222°, and cannot be distilled without decomposition. It is very similar to the cincholeupone obtained by Skraup (*Abstr.*, 1889, 282, 626). When heated with concentrated hydrogen bromide, it gives carbonic anhydride, a large quantity of resin, and an oily base which boils at 170—177°. It is easily converted into its alkyl ethers, which yield well-characterised hydrochlorides. The *nitroso-compound* does not give Liebermann's reaction, and evolves red fumes when boiled with hydrobromic acid. When treated with bromine water, a compound $C_9NH_4BrO_3 \cdot HBr$, is obtained, which is very similar to the compound obtained by Skraup from cincholeupone. E. C. R.

Organic Chemistry.

Stereoisomerism. By A. CLAUS (*J. pr. Chem.*, [2], **49**, 445—465).—A criticism of stereochemical theories, referring particularly to the recent exposition of the subject by V. Meyer (*Chem. Zeit.*, **17**, 1869).
A. G. B.

Action of Chlorine on Methane in Natural Gas. By F. C. PHILLIPS (*Amer. Chem. J.*, **16**, 361—365).—The gas consisted of methane (95.4 per cent.), carbonic anhydride (0.2 per cent.), nitrogen (4.4 per cent.), and a trace of oxygen. When a mixture of the gas with chlorine was passed over red-hot lampblack, methylic chloride and carbon tetrachloride were formed in abundance, whatever the proportions. Methylene chloride and chloroform were found only in small quantities. The methylic chloride resembled that prepared from methylic alcohol in all respects except one, that it failed to form a crystalline hydrate with ice-cold water. This confirms v. Baeyer's results (*Annalen*, **107**, 269). The author does not agree with Roscoe and Schorlemmer's view (*Chemistry*, [3], **1**, 203), that this is due to the presence of higher chlorides, as especial pains were taken to remove the latter.
JN. W.

Isomerides of Propylene and their Sulphates. By BERTHELOT (*Compt. rend.*, **118**, 10.9—10.13).—Propylene and trimethylene are both absorbed immediately by concentrated sulphuric acid at the ordinary temperature. A known weight of sulphuric acid was introduced into an eprouvette above some mercury, the latter acting as a conductor of heat, and thus preventing a rise of temperature. The dry gaseous hydrocarbon was gradually introduced into the vessel, and was absorbed at first rapidly and afterwards more slowly.

Trimethylene yields the normal sulphate (C_3H_7), SO_4 , which, on addition of water, separates as a heavy neutral oil, only very slightly soluble in water. The salt undergoes very little decomposition, even if left in contact with water for several weeks.

Trimethylene sulphate distils in water vapour, but, when heated alone, it decomposes into sulphurous anhydride, volatile liquids, and a carbonaceous residue. Potassium hydroxide decomposes it after heating for several hours in a sealed tube at 100°, sulphuric acid and propylic alcohol being formed.

The author points out that pure ethylene, unlike trimethylene, is very slowly absorbed by sulphuric acid.

Propylene under similar conditions is rapidly absorbed by sulphuric acid, and yields the sulphate, (C_3H_7), SO_4 , which resembles trimethylene sulphate in general physical properties, but is much less stable, and is dissolved and decomposed even by cold water in a few hours.

Isobutylene likewise yields a sulphate, (C_4H_9), SO_4 , which is gradually decomposed by water.

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C. H. B.
2 f

Production of Cyanides. By H. N. WARREN (*Chem. News*, 69, 186—187).—Attention is drawn to the small amounts of cyanide produced by igniting potassium nitrate with Rochelle salt or sodium acetate, or even when the nitrate is made into briquettes with wheat flour and magnesia and ignited; to the occasional inferiority of the product from thiocyanates; and to the value of the addition of lime or baryta when preparing cyanides by the incineration of nitrogenous compounds.
D. A. L.

Combination of Molybdenum Dioxide and Bisulphide with Alkali Cyanides. By E. PÉCHARD (*Compt. rend.*, 118, 804—807).—See this vol., ii, 319.

Ethylallylcarbinol. By H. FOURNIER (*Bull. Soc. Chim.*, [3], 11, 124—125).—A method of obtaining aromatic secondary alcohols by the action of allylic iodide and zinc on aldehydes has already been described by the author (this vol., i, 19). He now finds that the process is applicable to the fatty series, and that allylic bromide may be advantageously substituted for the iodide.

Ethylallylcarbinol, $C_3H_5\cdot CHEt\cdot OH$, is obtained by the action of allylic bromide on propaldehyde in presence of zinc turnings and dry ether. It is a colourless liquid, boiling at $130-132^\circ$; sp. gr. = 0.843 at 18° . The *acetate*, $C_3H_5\cdot CHEt\cdot OAc$, is a colourless liquid of an agreeable odour; it boils at $150-152^\circ$, and has sp. gr. = 0.891 at 18° .
M. O. F.

Chloralose. By A. PETIT and M. POLONOVSKI (*Bull. Soc. Chim.*, [3], 11, 125—133).—Heffter (*Abstr.*, 1889, 845) has already shown that chloralose and parachloralose are dextrogyrate. The authors have determined the rotatory power of chloralose, and find that for a 5 per cent. solution in 98 per cent. alcohol $[\alpha]_D = +19.4^\circ$ at $20-22^\circ$, whilst a solution in 4 per cent. potash gives $[\alpha]_D = +15^\circ$ at the same temperature.

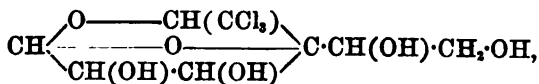
Contrary to the statement of Hanriot and Richet (this vol., i, 105), both chloralose and parachloralose reduce Fehling's solution on boiling, remaining indifferent towards ammoniacal silver nitrate. If, however, ammonia be added in sufficient quantity to redissolve the precipitate formed on adding sodium hydroxide to silver nitrate, a solution is obtained which is reduced by chloralose at a temperature of 70° .

Hot solutions of the alkalis eliminate chlorine from chloralose and parachloralose with the development of a brown coloration, and a similar result, accompanied by evolution of carbonic anhydride, is produced by sodium carbonate. When boiled for some hours with dilute baryta water, chloralose gives rise to products identical with those obtained on subjecting glucose and chloral to similar treatment, and the authors therefore conclude that under these conditions chloralose is first split up into glucose and chloral, these substances undergoing further decomposition in presence of the hot alkali. The behaviour of chloralose towards dilute acids fully confirms this view. When boiled for three hours with 20 per cent. sulphuric acid, chloral and glucose are formed, and if hydrochloric acid is employed, the re-

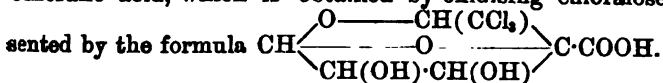
action proceeds almost quantitatively; hydrolysis is also effected when chloralose is boiled with distilled water.

Owing to its insolubility, parachloralose undergoes decomposition more slowly than the isomeric compound, although identical products are obtained.

The authors consider that the ease with which chloralose is broken up into glucose and chloral points to the constitution



this view being in agreement with the formation of tetra-substitution derivatives by the action of acids and acid chlorides on it (*loc. cit.*). Chloralic acid, which is obtained by oxidising chloralose, is represented by the formula



M. O. F.

Formation of Mannitol in Wines. By H. MALBOT and A. MALBOT (*Bull. Soc. Chim.*, [3], 11, 176—179; compare this vol., i, 269).—A description of the various hypothesis put forward to explain the formation of mannitol in wines. The paper is to be continued.

M. O. F.

Two new Hexitols and Compounds of the Polyvalent Alcohols with Benzaldehyde. By E. FISCHER (*Ber.*, 27, 1524—1537).—According to theory, 10 stereoisomeric forms of hexitol should exist, but only five have been hitherto obtained, namely, two mannitols, two sorbitols and dulcitol. The author has prepared two other members of the dulcitol series: the one, from *d*-talose, which is therefore termed *d*-talitol; the other, from dulcitol, is in all probability *i*-talitol. Talonic acid is prepared by the action of pyridine on galactonic acid in the manner previously described (*Abstr.*, 1892,

299). Hydroxymethylpyromucic acid, $\text{OH} \cdot \text{CH}_2 \cdot \text{C} \begin{array}{c} \text{CH} \cdot \text{CH} \\ \text{O} \text{---} \text{C} \cdot \text{COOH} \end{array}$, is formed in small quantity as a bye-product; it darkens at 160°, and melts at 165—170° with evolution of gas; its formation resembles that of pyromucic acid from arabonic acid (*Abstr.*, 1892, 437). Talonic acid is converted into a lactone on evaporation in aqueous solution, and from this *d*-talitol is formed by reduction with sodium amalgam; it is a colourless, slightly sweet syrup, sparingly soluble in ether. A 10 per cent. aqueous solution in a 10 cm. tube gives a refraction of +0.23°; on the addition of borax and alkali, this becomes -0.55°; these numbers are only approximate. The yield is 40 per cent. of the talonic acid employed. The tribenzal derivative, $\text{C}_6\text{H}_5\text{O}_6(\text{CHPh})_3$, crystallises from alcohol in slender, colourless needles; it softens at 200°, melts at 210° (corr.), and closely resembles tribenzalmannitol.

i-Talitol is prepared by the oxidation of dulcitol by means of lead peroxide and hydrochloric acid, and subsequent reduction of the

product with sodium amalgam. It crystallises in slender, concentric needles, melts at 66—67°, and is readily soluble in water and alcohol. The *tribenzal-derivative* crystallises from alcohol in slender, colourless needles, and melts at 210° (corr.). The yield is only 2—3 per cent. of the dulcitol employed. The compound so closely resembles tribenzal-d-mannitol that it was at first thought to be *tribenzal-i-mannitol*, the latter was therefore prepared for comparison; it melts at 190—192°.

A comparison of the benzal derivatives of the polyvalent alcohols shows that whilst their composition differs considerably, they are, with the exception of benzalsorbitol and benzalglycerol, formed under similar conditions. At present, it is impossible to decide what influence the configuration of the molecule exerts on the formation of these compounds. Benzal- α -glucoheptol, $C_7H_{14}O_7 \cdot CHPh$ (m. p. 218° corr.), has previously been prepared; under modified conditions, which are fully described, a labile modification is formed, which melts at 153—154° (corr., 155—156°); it is stable when dry, but under the influence of light and moisture, or on crystallisation from alcohol, changes rapidly into the stable form. The higher melting modification is readily soluble in hot water, not insoluble, as previously stated. *Dibenzaldulcitol*, $C_8H_{10}O_6(CHPh)_2$, is prepared by the interaction of benzaldehyde, dulcitol, and hydrogen chloride, or of hydrochloric acid at 0°, and crystallises from alcohol in slender needles melting and decomposing at 215—220° (uncorr.). It is readily resolved into its constituents on boiling with dilute acids. *Benzal-arabitol*, $C_8H_{10}O_6 \cdot CHPh$, prepared in a similar manner to the preceding compound, crystallises from chloroform, melts at 150° (corr., 152°), and is readily hydrolysed. *Dibenzalerythritol*, $C_8H_{10}O_4(CHPh)_2$, crystallises in slender needles, and melts at 197—198° (corr., 201—202°). It may be conveniently used for the identification of erythritol.

Benzalglycerol, $C_8H_{10}O_5 \cdot CHPh$, is prepared by the action of hydrogen chloride on benzaldehyde and glycerol at 0°, and crystallises from water in colourless, stellate needles melting at 66°. It has a bitter taste, distils in a vacuum without decomposition, and is immediately hydrolysed by the action of dilute acids. The benzalglycerol prepared 30 years ago by Harnitzky and Menschutkin was impure; it differed considerably from the author's compound, with which it is possibly isomeric.

Benzaltrimethyleneglycol, $CH_2 \begin{smallmatrix} CH_2 \cdot O \\ CH_2 \cdot O \end{smallmatrix} CHPh$, is prepared in a similar manner to the preceding compound, and is deposited from light petroleum in colourless crystals melting at 49—51°, and boiling at 125° (14 mm.). It is rapidly decomposed by dilute acids, but is unaffected by boiling with alkalis and phenylhydrazine in aqueous solution.

J. B. T.

Compounds of the Sugars with Polyhydric Phenols. By E. FISCHER and W. L. JENNINGS (*Ber.*, 27, 1355—1362).—It has been shown (this vol., i, 3) that the aliphatic alcohols react with certain sugars in presence of hydrochloric acid, forming glucosides; the

monohydric phenols, when subjected to the same treatment, remain unaltered. The experiments to be described show, however, that the polyhydric phenols yield compounds with certain sugars which differ widely according to the phenol employed. It has long been observed by Reichl, Molisch, Ihl, Selivanoff, Wheeler, and Tollens that various sugars give colour reactions with certain phenols in presence of hydrochloric or sulphuric acid. The products to be described are, however, colourless, and being obtained at a low temperature, the sugar molecule is preserved. The authors have not succeeded in obtaining the new substances in the crystalline condition, but having determined their composition with great probability, they are constrained to regard them as chemical individuals.

Resorcinol combines readily with all the aldoses with which the reaction has been tried; equimolecular proportions of the reagents give rise to compounds insoluble in alcohol, whilst when the amount of resorcinol is doubled, substances soluble in alcohol represent the main product.

Arabinose-resorcinol, $C_{11}H_{14}O_6$, is obtained by saturating an aqueous solution containing molecular proportions of arabinose and resorcinol with hydrogen chloride at a low temperature, and, after allowing it to remain for some hours at $0-10^\circ$, pouring the resulting reddish liquid into absolute alcohol. The compound is an amorphous, almost colourless powder having a faint taste; it dissolves readily in water, but very sparingly in alcohol, ether, benzene, chloroform, and glacial acetic acid, and decomposes at 275° . The compound remains unaltered when boiled with alkalis, and does not yield an osazone when heated with phenylhydrazine acetate; it exhibits, however, many reactions similar to those of resorcinol, thus: Its aqueous solution gives a bluish-violet coloration with ferric chloride, an insoluble bromo-derivative with bromine-water, and a colouring matter with diazobenzenesulphonic acid. Its solution in hydrochloric acid yields a condensation derivative with benzaldehyde.

Glucose-resorcinol, $C_{12}H_{16}O_7$, is obtained in a similar manner, although somewhat less readily than the arabinose derivative. It differs from the latter in being more easily hydrolysed by warm, dilute hydrochloric acid. Corresponding compounds are also obtained from xylose, galactose, and glucoheptose, but these were not analysed.

In the case of the ketoses, fructose, and sorbinose, a dark red, insoluble compound is formed, even at a low temperature, which is probably identical with the product obtained by Ihl, and later by Selivanoff (Abstr., 1887, 459).

Detection of Carbohydrates by means of Resorcinol.—The compounds of resorcinol just described give beautiful, magenta colorations when treated with oxidising agents in alkaline solution. The reaction with Fehling's solution is very delicate, and appears to be available for all carbohydrates. The *modus operandi* recommended by the authors is as follows:—To the dilute aqueous solution of the substance to be tested (2 c.c.), resorcinol (0.2 gram), is added to the mixture saturated with hydrogen chloride at 0° . When the amount of carbohydrate is small, the test is allowed to remain at the ordinary temperature for 12 hours; if, however, it is large, one hour suffices.

It is diluted with water, an excess of sodium hydroxide added, and warmed with Fehling's solution, of which latter only a few drops are taken when the amount of carbohydrate is small. A reddish-violet coloration ensues, which is very characteristic; it is fugitive after a time when the liquid is largely diluted. Insoluble carbohydrates, such as starch, are triturated with water, and, after the addition of resorcinol, hydrogen chloride is passed into the cooled mixture. The reaction has been found available for the detection of small quantities of saccharose, lactose, maltose, dextrin, gum, glycogen, starch, and cotton-wool; normal urine exhibits the reaction in a marked degree. It is to be recommended as a confirmatory test to that of Molisch (Abstr., 1886, 923).

Catechol reacts with the aldoses much more slowly than does resorcinol, and in the case of the quinol, which is very sparingly soluble in concentrated hydrochloric acid, no action on the sugars was observed.

Orcinol reacts with glucose more readily than does resorcinol, but the product is insoluble in water, and apparently of a complex nature.

Arabinose-pyrogallol, $C_{11}H_{14}O_7$, is obtained in the same manner as the resorcinol derivative; it is an almost colourless compound, decomposes at 240° , behaves with alkalis as pyrogallol, and gives a beautiful blue coloration with ferrous sulphate. *Glucose-pyrogallol* was also prepared.

A. R. L.

Blue Iodide of Starch. By Miss C. F. ROBERTS (*Amer. J. Sci.*, [3], 47, 422—429).—With a view of determining between the views of Mylius (Abstr., 1887, 568) and Stocks (Abstr., 1888, 126 and 668), the authoress has experimented on this subject. When blue iodide of starch is precipitated, well washed with dilute sulphuric acid, and then iodic acid added, the solid dissolves to a colourless liquid, although the presence of free iodine therein can be proved by shaking with chloroform. A single drop of a weak solution of silver nitrate is enough to destroy the deep blue colour of a test-tube full of liquid. Both these experiments point to the discharge of colour being due to the removal of hydriodic acid rather than of iodine. The authoress has been unable to obtain an aqueous solution of iodine perfectly free from hydriodic acid. If, however, a chloroform solution of iodine is well washed with water to free it from hydriodic acid, and then immediately shaken with pure water and starch emulsion, no coloration is produced. The addition of a little hydrochloric acid, or of potassium iodide, or heating the liquid, or exposing it to sunlight (the latter two operations, of course, causing the formation of traces of hydriodic acid) at once causes the blue coloration to appear. When iodine chloride is added to starch-blue, the blue colour is discharged, but iodine at the same time set free. The reaction is probably $HI + ICl = HCl + I_2$, the hydriodic acid being taken from the starch-blue. The fact that considerable quantities of iodic acid must be added to liquids containing starch-blue before the colour is discharged is probably due to the fact that, as shown by Landolt and others, the reaction between hydriodic and

iodic acids in dilute solution is very slow, and that in an aqueous solution of iodine in the light, traces of hydriodic acid are being constantly formed. Her experiments lead the authoress to support Mylius' formula, $(C_6H_{10}O_5I)_nHI$, for starch-blue. L. T. T.

Natural Oxycelluloses. By G. DE CHALMOT (*Ber.*, 27, 1489—1491).—The author (Abstr., 1893, ii, 430; *Amer. Chem. J.*, 16, 218) has made experiments similar to those of Cross, Bevan, and Beadle (this vol., i, 354). The substances in plants which, on simple hydrolysis, yield furfuraldehyde, he considers to be pentosans. He has shown with regard to these that (1) both the absolute and the relative quantity increase when maize or peas germinate in the dark; (2) the quantity in the seed is partly transferred to the young plant; (3) in the germination of the seeds of *Tropæolum majus* the absolute amount decreases; (4) the percentage amount increases in various organs of living plants; (5) the percentage amount shows no regular decrease or increase after the lignification is complete; (6) in the case of 30 different trees, the presence of these substances is not essential to lignification. C. F. B.

New Constituents of Wood Oil. By E. LOOFT (*Ber.*, 27, 1542—1546; compare Abstr., 1893, i, 558).—The author has succeeded in separating the following compounds from crude wood oil; they were identified by their boiling points, the analytical results, and the preparation of characteristic derivatives: methylpyridine, dimethylpyridine, (iso)butylic alcohol, pimelic ketone, and an alcohol of the formula $C_8H_{14}O$. Full details of the methods of separation employed are given in the original paper. The sp. gr. of pimelic ketone = 0.9416, refractive coefficient for sodium light = 1.443 at 24°; the molecular refractive power = 27.58. J. B. T.

Nitramines. By A. LACHMAN and J. THIELE (*Ber.*, 27, 1519—1520).—The nitramines of several of the simplest of the acid amides cannot be obtained by the method adopted by Franchimont (*Rec. Trav. Chim.*, 2, 95, 340; 3, 219) for the preparation of other nitramines. If, however, only the theoretical amount of nitric acid be taken, the nitrate of the amide being employed when one exists, these derivatives can be prepared quite readily.

Nitrocarbamide, $NO_2 \cdot NH \cdot CO \cdot NH_2$, is precipitated when a solution of carbamide nitrate in sulphuric acid is poured upon ice. It forms a powder, which is sparingly soluble in cold water and alcohol, more readily on warming. It is a strong acid, expels carbonic anhydride, and forms neutral alkali salts. When warmed with alkalis, it is decomposed and gas is evolved; mercuric and mercurous nitrates produce sparingly soluble compounds. When reduced, it yields a small amount of semicarbazide.

Nitro-urethane, $NO_2 \cdot NH \cdot COOEt$, is obtained by adding the calculated amount of nitric acid to a solution of urethane in sulphuric acid. It crystallises from light petroleum in splendid plates, melts at 64°, and is readily soluble in most solvents. An ammonia derivative $NH_3 \cdot NO_2 \cdot NH \cdot COOEt$, melts at 183°.

Dicyanodiamide and biuret yield similar derivatives, which are being further investigated. A. H.

Isonitramines. By W. TRAUBE (*Ber.*, 27, 1507—1510).—When dry nitric oxide is passed into a 10 per cent. alcoholic solution of ethylic sodacetacetate, the gas is absorbed, and a sodium salt is precipitated. This salt separates from aqueous solution on the addition of alcohol and ether in white, lustrous plates, of the composition $C_4H_5N_2O_5Na_2 + H_2O$. It is very readily soluble in water, yielding an alkaline solution. Silver nitrate produces a white precipitate, which decomposes with evolution of gas and separation of silver when the liquid is heated. The sodium salt decomposes with a gentle explosion when it is heated. Dilute acids decompose the salt slowly in the cold, violently when heated, a mixture of nitrogen and nitrous oxide being evolved. This salt probably belongs to the same class of substances as the salts of dinitrosulphonic acid, $H_2N_2SO_5$, and of the dinitroalkylic acids, such as EtN_2O_5H . It has the composition of a nitramine, and may, therefore, be provisionally termed an *isonitramine*.

Similar compounds may be obtained from ethylic benzoylacetate, ethylic malonate, benzoylacetone, and monoketones, such as acetone.

The *acetone*-compound, $CH_3(N_2O_5Na)_2$, is formed, together with sodium acetate, when nitric oxide is passed into an alcoholic solution of acetone to which caustic soda or sodium ethoxide has been added. A yellow sodium salt is formed from which the *barium* salt, $CH_3(N_2O_5)_2Ba + 3H_2O$, may be prepared. This forms lustrous, colourless needles, and is almost insoluble in cold water, but dissolves sparingly in hot water yielding a neutral solution. The dry compound explodes when heated, and is decomposed by acids. Acetophenone yields the same compound along with benzoic acid. The substance, $CH_3(N_2O_5)_2H$, from which these salts are derived, may be termed *methylenedi-isonitramine*. The investigation of these compounds is being continued. A. H.

Dimethylarsine. By A. W. PALMER (*Ber.*, 27, 1378—1379).—*Dimethylarsine*, $AsHMe_2$, has been obtained, for the first time, by reducing cacodyl chloride with platinised zinc and alcoholic hydrogen chloride. It is a colourless, mobile liquid, boiling at 36—37° (uncorr.); it inflames spontaneously in air, and is decomposed by silver nitrate solution, silver being precipitated and, apparently, cacodylic acid formed. C. F. B.

Natural Unsaturated Ketone. By P. BARBIER and L. BOVEAULT (*Compt. rend.*, 118, 983—986).—Oil of lemon grass, according to Dodge, contains geranaldehyde, $C_{10}H_{16}O$. The authors find that by fractionation under a pressure of 12 mm. the oil can be separated into a fraction boiling at 67—75°, another boiling at 110—115°, and a third consisting of a brown, viscous liquid, which has not yet been investigated. The lowest fraction, which under ordinary pressure distils completely at 170—175°, is generally regarded as consisting of a terpene, but the authors find that it usually consists of a mixture of

a non-saturated ketone and a terpene. The ketone when separated by means of the bisulphite compound, has the composition $C_8H_{14}O$, and boils at $169-170^\circ$ under ordinary pressure; sp. gr. at $0 = 0.8632$; refractive index at 15.6° , $n_{D_{15.6}} = 1.4608$, $n_{D_{25.6}} = 1.4760$; molecular weight by Raoult's method, 125.7. With potassium iodide and sodium hypobromite the ketone yields iodoform, and this, together with the formation of a bisulphite compound, indicates the presence of the $\cdot COMe$ group. With chromic acid mixture, the ketone yields carbonic anhydride, acetone, formic acid, and acetic acid, and hence it would seem that it is *methyl hexylene ketone*, $CMe_3 \cdot CH \cdot CH_2 \cdot CH_2 \cdot COMe$. It differs in chemical and physical properties from the methyl hexylene ketone obtained by synthesis (this vol., i, 224), and is not identical with that obtained by Wallach by the distillation of cinoleic anhydride, nor with that obtained by Tiemann and Semmler by the oxidation of geraniol and geranaldehyde.

The terpene sometimes associated with this methyl hexylene ketone, boils at 175° , and has a rotatory power $[\alpha]_D = -5^\circ 48'$. It combines with exactly 4 atoms of bromine, but the bromo-derivative yields only a very small quantity of crystals melting at 85° , and hence the terpene is not a limonene. The absence of this terpene in some cases, and the great variation in its proportions in others, indicates that it is added for the purpose of adulteration.

C. H. B.

The Aldehyde from Oil of Lemon grass. By P. BARBIER and L. BOUVEAULT (*Compt. rend.*, 118, 1050—1052).—When geranaldehyde is treated with chromic acid mixture at a low temperature, it yields formic and acetic acids and a methylhexyleneketonecarboxylic acid, $C_8H_{14}O \cdot COOH$, which yields iodoform when mixed with potassium iodide and sodium hypobromite. This acid would seem to be identical with the oily acid obtained by Tiemann and Semmler, which yielded methyl hexylene ketone when distilled.

When oxidised by means of boiling chromic acid mixture, geranaldehyde yields carbonic anhydride, acetone, acetic acid, and terebic acid, $C_7H_{12}O_8$. When boiled with three times its weight of glacial acetic acid for 24 hours, geranaldehyde is converted into cymene.

It would follow from these reactions that geranaldehyde has the constitution $CH_3 \cdot CMe \cdot CH_2 \cdot CH_2 \cdot C \cdot (COH) \cdot CMe_3$, and not that ascribed to it by Tiemann and Semmler (this vol., i, 82). Its conversion into cymene can be explained by assuming that the acetic acid first acts as a hydrating and afterwards as a dehydrating agent.

C. H. B.

Crystallographic Properties of the two Stereoisomeric α -Methyl- β -chlorocrotonic acids from α -Dichloro-*s*-dimethylsuccinic acid. By R. OTTO (*Ber.*, 27, 1351—1352).—The α -methyl- β -chlorocrotonic acid melting at $50-60^\circ$ (this vol., i, 318) crystallises from water in six-sided, biaxial laminæ showing straight extinction; it therefore does not answer the description given by Brugnatelli and by Kloos.

The isomeric acid melting at 73° is obtained in transparent, glassy, monosymmetric crystals of variable habit:

$$a : b : c = 0.9232 : 1 : 1.2421. \quad \beta = 83^\circ 23'.$$

These results agree with those of Kloos.

W. J. P.

Formation of Pyruvic acid in an Aqueous Solution of Tartaric acid independently of Micro-organisms. By R. OTTO (*Ber.*, 27, 1264—1265).—A careful examination of the solution of tartaric acid which contained pyruvic acid after being kept for some years (this vol., i, 274), has proved the absence of micro-organisms.

E. C. R.

Preparation of Glyoxylic acid. By C. BÖTTINGER (*Arch. Pharm.*, 232, 65—69).—Debus's method of preparing glyoxylic acid is modified in regard to the proportions of alcohol and nitric acid employed, 50 c.c. of absolute alcohol being separated by a layer of 27 c.c. of water from 100 c.c. of nitric acid (sp. gr. 1.48) at 5°; when complete mixture has taken place, ethylic nitrite is removed by distillation, and glyoxylic acid can then be separated from the residual liquid in the usual manner.

A calcium salt of the formula $(C_2H_3O_4)_2Ca + H_2O$ separates slowly from cold dilute solutions; it becomes anhydrous at 110°. When boiled with acetic anhydride, glyoxylic acid forms an *acetate*, a gum-like substance which is gradually resolved into acetic acid and glyoxylic acid by cold water.

M. O. F.

Detection of Glyoxylic acid. By C. BÖTTINGER (*Arch. Pharm.*, 232, 1—3).—Glyoxylic acid forms with dimethylaniline a colourless condensation product, readily soluble in a dilute solution of caustic soda, from which it is precipitated by dilute acetic acid in slender, colourless needles; when boiled with an aqueous solution of mercuric chloride, a deep blue coloration is developed.

The liquid obtained by warming glyoxylic acid and resorcinol with a small quantity of absolute alcohol, gives, on dilution with water and careful addition of ammonia, a deep blue colour which soon becomes bright red; when caustic soda is employed, the final tint is cherry red. If a mixture of glyoxylic acid and resorcinol is heated on a water bath with concentrated sulphuric acid, evolution of carbonic anhydride takes place, and a substance is obtained which is scarcely soluble in water or dilute caustic soda.

An ammoniacal solution of the compound formed on adding glyoxylic acid to β -amidoalizarin dissolved in concentrated sulphuric acid, has a deep violet-red colour. A brown, crystalline substance has been obtained by adding glyoxylic acid to an alcoholic solution of α -naphthylamine.

The author has studied the action of ammonium hydrosulphide on dichloroacetic acid, obtaining a *lead salt* of the constitution



The acid formed on decomposing this salt with hydrogen sulphide or sulphuric acid is extremely volatile and unstable. It gives rise to a volatile *ethylic salt*, which possesses a penetrating, garlic-like odour, and forms a colourless compound with phenylhydrazine.

M. O. F.

Conversion of Ethylic Dioxysuccinate into Ethylic Oxymalonnate and Ethylic Oxalate by elimination of Carbonic Oxide. By R. ANSCHÜTZ and H. PAULY (*Ber.*, 27, 1304—1306).—In the preparation of ethylic dioxysuccinate from sodium tetrahydroxysuccinate, alcohol, and hydrogen chloride, the authors observed that, during the distillation of the product, decomposition set in, and ethylic oxymalonnate and ethylic oxalate were formed. The same two compounds are most easily obtained from ethylic dioxysuccinate by heating it at 125° under a pressure of 12 mm. with a small quantity of the tarry residue obtained in a previous decomposition. The same decomposition takes place less readily when ethylic dioxysuccinate is heated alone at 280—290°. Carbonic oxide is evolved in large quantities during the decomposition. When ethylic oxymalonnate is heated at 180° under 12 mm. pressure, carbonic oxide is evolved and ethylic oxalate is formed.

Ethylic dioxysuccinate, oxymalonnate, and oxalate are therefore the first members of an homologous series of compounds in which the homology is determined by the carbonyl group. E. C. R.

Anomalous Condensations. By C. A. BISCHOFF and P. WALDEN (*Ber.*, 27, 1491—1495).—Reactions have been studied in which condensation takes place accompanied by linkage (i) of C with C, as in the case of ethylic sodiomethylmalonnate with ethylic α -bromoisobutyrate; (ii) of C with N, as of (a) piperidine with ethylic α -bromopropionate, or of (b) aniline with chloracetamide; (iii) of C with O, as of sodium orthonitrophenoxide with ethylic α -bromopropionate. Many anomalous cases were observed; these may be put into three categories: (A) the condensation takes place, not at the α - but at the β -position, or mainly in this position; (B) condensation takes place not between unlike, but between two like molecules; (C) no condensation occurs. The paper is a preliminary one, and must be consulted for further details. C. F. B.

Behaviour of Maleic acid on heating. By S. TANATAR (*Ber.*, 27, 1365—1368).—The author's experiments show that when maleic acid is heated with benzene, it is directly converted into fumaric acid; maleic anhydride and, consequently, also water are likewise produced. The formation of malic acid observed by Skraup (this vol., i, 15) is to be attributed to the interaction of fumaric acid and water at the high temperature. Contrary to Skraup's observation, when dry maleic acid is heated at 180—190°, no malic acid is found. A. R. L.

Conversion of Citraconic acid into Mesoconic acid. By R. FRANZ (*Monatsh.*, 15, 209—227).—The author has carried out with citraconic acid experiments similar to those made by Skraup (*Abstr.*, 1891, 1338; and this vol., i, 15) with maleic acid. When an aqueous solution of citraconic acid was heated at 120°, some itaconic acid was formed; when heated at 180—200°, it was partially converted into mesoconic acid. Neither at these nor intermediate temperatures could any change of titre (formation of lactone) be observed. Neither hydrogen sulphide nor sulphurous anhydride alone has any effect on citraconic acid, but when these two compounds are allowed

to act together on a solution of the acid, a small proportion thereof is converted into mesaconic acid. When the copper and lead salts are decomposed by hydrogen sulphide, mesaconic acid is formed in small quantities, the lead salt yields, however, much less than the copper salt. No mesaconic acid was formed by heating copper citraconate to incipient decomposition.

Mineral acids act much more energetically in bringing about this change, the quantity of mesaconic acid formed being larger the stronger the solution of mineral acid, the greater the proportion of such solution used, and the longer the heating is continued. The amount of conversion is in all cases much smaller than is the case with maleic acid.

For the purpose of this research, the author investigated the methods of separation of itaconic, citraconic, and mesaconic acids. He found that the data generally given as to the behaviour of these acids to steam distillation are incorrect, for whilst citraconic acid is much the most volatile in steam, the other two acids also pass over in quantities too appreciable to enable this method to be used for quantitative separation. The author took advantage of the different solubilities of these acids in water and ether. In water, mesaconic is by far the least soluble, citraconic by far the most soluble, whilst in ether the order of solubility is exactly reversed. By treating an aqueous solution containing the mixed acids with its own volume of ether, almost the whole of the mesaconic acid, and but very little of the citraconic acid is removed. The ether is distilled off, the residue dried over sulphuric acid and any citraconic acid removed by rubbing on a porous plate with a trace of water or by washing with a concentrated solution of mesaconic acid. The percentage of mesaconic acid so obtained is always much below that present, but the process is available as an indication of the relative quantities converted in different reactions.

L. T. T.

Propionyl Derivatives of Ethylic Mucate. By P. FORTNER and Z. H. SKRAUP (*Monatsh.*, 15, 200—208).—When ethylic mucate is digested in a reflux apparatus with propionic chloride, *ethylic tetrapropionylmucate*, $\text{COOEt}[\text{CH}\cdot\text{O}\cdot\text{COEt}]_4\cdot\text{COOEt}$, is obtained, which forms colourless transparent crystals, melts at $118-120^\circ$, and is easily soluble in ether, acetone, benzene, glacial acetic acid, and boiling alcohol. If the digestion is carried on, however, in sealed tubes at 100° , *ethylic tripropionylmucolactone*, $\text{COOEt}[\text{CH}\cdot\text{O}\cdot\text{COEt}]_3\cdot\text{CH} < \begin{smallmatrix} \text{O} \\ \parallel \\ \text{CO} \end{smallmatrix}$, is

formed, together with some of the tetrapropionyl compound. This lactone yields colourless crystals, melting at $56-58^\circ$, and easily soluble in ether. The constitution of these two compounds was established by estimations of the propionyl and ethoxyl groups. When hydrolysed with acids, both yielded mucic acid, and with alkalis the isomeric acids found by Skraup (this vol., i, 16) in the similar treatment of ethylic tetracetylmucate were obtained.

In view of these results the authors have re-examined the corresponding acetyl reaction (*loc. cit.*), and find that the compound then described by Skraup as β -ethylic tetracetylmucate is really ethylic

triacetylmucolactone, for which the percentage composition is almost identical with that of the tetracetyl compound. L. T. T.

Method for obtaining Carbamides containing Tertiary Alkyl Radicles. By A. SCHNEEGANS (*Arch. Pharm.*, 231, 675—680).—The method consists in heating the bromide of the tertiary alcohol with a mixture of white lead (as a source of lead hydroxide) and carbamide.

Tertiary butylcarbamide $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}_3$, crystallises in needles, melts and partially decomposes at 172° , and dissolves sparingly in cold water, but freely in alcohol.

Tertiary amylcarbamide, already described by Würtz, was similarly prepared; it melts at $151\text{--}152^\circ$; its crystallography is described.

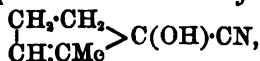
Tertiary heptylcarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_{15}$, crystallises in needles, decomposes at 150° , and is nearly insoluble in cold water, but fairly soluble in boiling water.

The solubility of these carbamides in cold water decreases with increase of molecular weight, the proportion of water requisite for the solution of one part of each of the three respectively, in the above order, being 46.3, 79, and 410 parts. A. G. B.

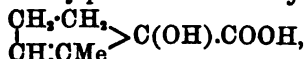
Methylketopentamethylene and its derivatives, and Symmetrical Ketopentamethenylene. By E. LOORT (*Ber.*, 27, 1538—1542).—An additive compound of sodium hydrogen sulphite with α -methyl- β -ketopentamethenylene, has been previously described (*Abstr.*, 1893, i, 558), from this the ketone is regenerated on heating with acids, or by the action of alkalis at ordinary temperatures.

1-Methyl-5-hydroxypentamethylene, $\text{CHMe} < \begin{smallmatrix} \text{CH}(\text{OH})\cdot\text{CH}_2 \\ \text{CH}_2\text{---CH}_2 \end{smallmatrix}$, is formed by the reduction of the keto-compound with sodium in moist ethereal solution, it is a colourless mobile liquid, with an odour resembling that of iodoform, it boils at $148\text{--}149^\circ$; the sp. gr. = 0.9273 at 14.5° ; the coefficient of refraction for sodium light = 1.4475; molecular refractive power = 28.84.

The *pinacone* $\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}\cdot\text{CMe} \end{smallmatrix} > \text{C}(\text{OH})\cdot\text{C}(\text{OH}) < \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CMe}\cdot\text{CH} \end{smallmatrix}$ is obtained with the preceding compound, and is a thick, pale yellow liquid boiling at 330° , and remaining liquid at -20° . The *hydroxynitrile*,



is prepared by the action of hydrogen cyanide on the ketone in aqueous solution, it crystallises in long needles, melts at 49° , boils at 213° under 300 mm. pressure, and, with slight decomposition, at 240° (corr.) under ordinary pressures. The *hydroxy acid*,



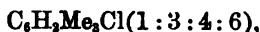
is formed quantitatively from the nitrile by hydrolysis with hydrochloric acid, it is crystalline, very readily soluble, and melts at $87\text{--}88^\circ$. The salts are amorphous and readily soluble.

Symmetrical ketopentamethenylene, $\text{CO} < \begin{smallmatrix} \text{CH}_2\cdot\text{CH} \\ \text{CH}_2\cdot\text{CH} \end{smallmatrix}$, prepared by the distillation of calcium Δ^3 -dihydromuconic acid, is a colourless liquid, and, like the oxime, readily combines with bromine. The *oxime* and its *hydrochloride* are oily. J. B. T.

Hexachlorobenzene Dichloride. By E. BARRAL (*Compt. rend.*, 118, 1049).—When hexachlorophenol, $\text{C}_6\text{Cl}_6\text{O}$, is heated in a sealed tube at 150 — 155° for 24 hours with phosphorus pentachloride, *hexachlorobenzene dichloride*, C_6Cl_8 , is formed, and is purified by crystallisation from light petroleum. It forms long, colourless prisms, which melt to a colourless liquid at 159 — 160° , but decompose into chlorine and hexachlorobenzene at a higher temperature. It dissolves readily in anhydrous ether, benzene, and alcohol, especially on heating, and is also somewhat soluble in hot light petroleum. A boiling aqueous solution of sodium hydroxide neither dissolves nor decomposes it; fuming nitric acid dissolves it slowly on heating, and when water is added a white precipitate separates and the liquid contains chlorine.

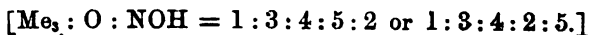
C. H. B.

Derivatives of Pseudocumene. By R. NIETZKI and J. SCHNEIDER (*Ber.*, 27, 1426—1432).—*Dinitrochloropseudocumene*, $\text{C}_6\text{Me}_3\text{Cl}(\text{NO}_2)_2$, is prepared by the direct nitration of chloropseudocumene,

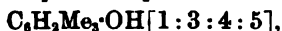


and forms almost colourless needles, melting at 205 — 206° . Although this substance contains a chlorine atom in the ortho-position to a nitro-group, it does not react with alcoholic ammonia or aniline. *Paradiamidochloropseudocumene* forms slender needles, melting at 171° . When a solution of a salt of this base is treated with ferric chloride, *chloropseudocumoquinone* is obtained in slender golden-yellow needles, melting at 72 — 73° . Sulphurous acid reduces it to the *quinol*, which melts at 202° , a *quinhydrone*, melting at 154° , being formed as an intermediate product in dark needles with a metallic lustre. The *quinol* yields a *diacetate* melting at 172° .

Paradinitropseudocumene is prepared from dinitropseudocumidine by the diazo-reaction; it forms orange-yellow needles, melting at 96° . *Paradiamidopseudocumene* was obtained in the form of the hydrochloride by the reduction of the foregoing substance. On oxidation, it yields a *pseudocumoquinone*, which crystallises in long yellow needles, and melts at 32° , and thus differs from that obtained by Noelting and Baumann (*Ber.*, 18, 1152) from isoduridine, which melted at 11° . On reduction, it is converted into a *quinol*, which melts at 170° , and is apparently identical with that obtained by Noelting and Baumann. The *diacetate* melts at 112° . The difference between the two quinones is probably due to some impurity in that prepared from isoduridine. *Pseudocumoquinonoxime* crystallises in long golden-yellow needles, and melts at 184° . A dioxime could not be obtained. *Pseudocumoquinonoxime* may have either of the following formulæ:



In order to decide this question, pseudocumenol,



was treated with nitrous acid. The nitroso-compound thus produced, which must have the constitution shown by the first formula, melts at 134° , and is odourless, and therefore differs from the pseudocuminoquinoxime, which, as stated above, melts at 184° , and, moreover, has an intense odour of quinine. This substance seems therefore to have the second of the two formulæ. A. H.

Additive Products of the Aromatic Isocyanides. By W. R. SMITH (*Amer. Chem. J.*, 16, 372—393).—Paratolylic isocyanide is a colourless crystalline solid, which melts at 21° to a colourless oil, and boils at 99° under 32 mm. pressure. Its odour is less disagreeable than that of phenylic isocyanide; its taste is extremely bitter. In the liquid form, it soon decomposes and polymerises, but is fairly stable in the solid form. Sulphur (in carbon bisulphide solution at 120 — 140°) converts it into the corresponding thiocarbimide, melting at 26° and boiling at 242 — 243° . The tendency to form this compound is so great that the isocyanide will take up sulphur from a carbon bisulphide solution of bromine and from vulcanised indiarubber.

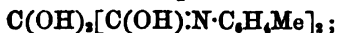
The isocyanide interacts with sulphur monochloride to form the thiocarbimide and *paratolylimidocarbonic chloride*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{CCl}_2$.

With hydrogen sulphide, in alcoholic solution at 100° , the isocyanide yields *paratolylimidothioformic acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{CH}\cdot\text{SH}$, which crystallises in nearly colourless flat needles, and melts at 175 — 176° . With ethylmercaptan at 100° , it yields the *ethylic salt* of this acid, a slightly yellow oil of disagreeable odour, boiling at 250 — 252° .

With alcoholic sodium ethoxide at 120° , the isocyanide yields *ethylic paratolylimidoformate*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{CH}\cdot\text{OEt}$, a pleasant-smelling yellow oil, which boils at 231 — 232° under 743 mm. pressure, and solidifies to a crystalline substance, melting at 8° . The *methylic salt* is made in a similar manner, and boils at 216 — 218° . Both salts are converted by hydrochloric acid into diparatolylformamidine hydrochloride. The amidine also results from direct interaction between the isocyanide and paratoluidine at 200° , or alcoholic paratoluidine at the ordinary temperature.

The isocyanide is reduced by nascent hydrogen (sodium in amyllic alcohol) to methylparatoluidine.

Paratolylic isocyanide interacts with carbonic chloride in ethereal solution at -18° to form *mesoxalodiparatoluidide hydrate*,



this crystallises in colourless needles and melts at 120 — 130° when quickly heated. When slowly heated, it loses its water of hydration and melts at 187° . It has slightly acid properties as it dissolves in alkalis, and is reprecipitated by acids. With alcohol, it forms the corresponding *alcoholate*. This, on heating, loses alcohol and leaves the anhydrous amide. The latter interacts with phenylhydrazine, but the product has not been examined.

With benzoic chloride, the isocyanide reacts at 100° to form *benzoylformoparatoluidide*, $\text{COPh}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, which crystallises in

yellow needles and melts at 111—113°; with acetic chloride it forms *pyruvoparatoluidide*, $\text{OH}\cdot\text{C}\cdot\text{Ac}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Me}$. This crystallises in colourless scales and melts at 108°; it forms a polymeride melting at 193—194°. The *phenylhydrazone* melts at 204°. With formic acid the isocyanide yields formoparatoluidide.

Paratolylic isocyanide forms, with silver cyanide, a crystalline molecular compound, $2\text{AgNC}\cdot 3\text{C}_6\text{H}_4\cdot\text{NC}$, which melts and decomposes at 118°.

Isocyanides easily take up two atoms of chlorine, forming alkylated imidocarbonic chlorides, and these interact with sodium alkyl-oxides to form alkylated imidochloroformates and imidocarbonates. *Phenylimidocarbonic chloride*, $\text{NPh}\cdot\text{CCl}_2$, is most conveniently made by the action of chlorine on the thiocarbamide.

Ethylic phenylimidochloroformate, $\text{NPh}\cdot\text{CCl}\cdot\text{OEt}$, is best obtained by mixing an alcohol-ether solution of the carbonic chloride with alcoholic sodium ethoxide. It is a colourless, sweet-swelling oil, which boils at 105° under a pressure of 12 mm., and has a sp. gr. of 1.144 at 12°. It is violently decomposed by strong hydrochloric acid into phenylic isocyanate and ethylic chloride. The isocyanate undergoes a secondary change into carbanilide. The *methylic salt* boils at 104° under 15 mm. pressure and at 215°, decomposing slightly, under ordinary pressure. The *phenylic salt* boils at 168° under 12 mm. pressure, and solidifies to a white substance, melting at 43°. It is hydrolysed by hydrochloric acid into phenylic phenylcarbamate. With aniline, it forms α -triphenylguanidine. When double the quantity of sodium ethoxide required to form the chloroformate is used, *diethylic phenylimidocarbonate*, $\text{NPh}\cdot\text{C}(\text{OEt})_2$, is obtained as a colourless, and nearly odourless, oil, which boils and decomposes slightly at 245°. It is hydrolysed by cold dilute hydrochloric acid into aniline and ethylic carbonate. The *methylic salt* boils at 123.5° under 16 mm. pressure. It interacts with aniline to form carbanilide.

JN. W.

Diphenylic Thiocarbonate. By H. ECKENBOTH and K. KOCK (*Ber.*, 27, 1368—1371).—*Diphenylic thiocarbonate*, $\text{CS}(\text{OPh})_2$, is obtained by dropping thiocarbonic chloride into an aqueous solution of sodium phenoxide; it crystallises from alcohol in white leaflets, melts at 106°, boils and decomposes slightly at 336—340°, and is insoluble in water. When heated with bromine and water at 120°, a *dibromo-derivative*, $\text{C}_{12}\text{H}_8\text{Br}_2\text{O}_2\text{S}$, is obtained; this forms white needles, melts at 177°, and gives parabromophenol on hydrolysis with soda. By the action of ammonia or amines on diphenylic thiocarbonate, carbamide derivatives are obtained. When heated with sodium ethoxide, it yields ethylic sulphide, phenol and carbonic anhydride. *Phenylic phenylthiocarbamate*, $\text{C}_{12}\text{H}_{11}\text{NSO}$, is obtained by distilling diphenylic thiocarbonate with thiocarbamilide, and allowing the oily product to remain for two months; it forms white crystals, and melts at 147°. When diphenylic thiocarbonate is heated with paratolylthiocarbamide, *paratolylthiocarbimide* and phenol are the products. Diphenylic carbonate (m. p. 78°) is formed when mercuric oxide is added to fused diphenylic thiocarbonate.

A. R. L.

Synthesis of Benzoylphloroglucinol Trimethyl Ether. By G. CIAMICIAN and P. SILBER (*Ber.*, 27, 1497—1501; compare this vol., i, 255).—Benzoylphloroglucinol trimethyl ether, $C_6H_2(OMe)_3COPh$, may be synthetically obtained by heating phloroglucinol trimethyl ether in benzene solution with benzoic chloride and zinc chloride. It melts at 115° , and has all the properties of the naturally occurring methylhydrocotoin or benzoylhydrocotoin (m. p. 113°). It crystallises, however, in large plates, whilst the natural product usually occurs in needles or prisms. A crystallographic comparison of the two products shows that the constants of the two types of crystal are identical. Both the natural and the synthetical products usually crystallise in monosymmetric forms, but also sometimes occur in rhombic crystals of the same melting point.

Dibenzoylphloroglucinol trimethyl ether, $C_6H(OMe)_3(COPh)_2$, is obtained when an excess of benzoic chloride is used, and forms white needles, melting at 179° . It is sparingly soluble in alcohol, insoluble in water and alkalis, and gives no coloration with nitric acid.

The authors give the name of coto-substances to those constituents of coto bark which are derived from phloroglucinol, the constituents derived from phenylcoumalin being known as paracoto-substances.

A. H.

Reduction of Nitro-compounds. By A. WOHL (*Ber.*, 27, 1432—1437).—The author has obtained results similar to those described by Bamberger (this vol., i, 373). The reduction of nitrobenzene by the aid of zinc-dust and water proceeds much more readily when the nitrobenzene is dissolved in alcohol of 60 per cent. and about 10 per cent. of calcium chloride added. The mass boils up at each addition of the zinc-dust, and by using the calculated amount of zinc-dust, a yield of about 75 per cent. on the nitrobenzene is obtained. The calcium chloride appears to aid the reaction by forming an insoluble basic salt with the zinc hydroxide, and thus preventing it from hindering the course of the reduction. The phenylhydroxylamine thus obtained has already been described by Bamberger. It readily combines with aldehydes and with phenylthiocarbimide, yields ethylic derivatives with ethylic iodide and sodium ethoxide, and is converted by nitrous acid into the sparingly soluble *nitroso-phenylhydroxylamine*, $OH \cdot NPh \cdot NO$. This forms slender, white needles, melts without decomposing at 58 — 59° , and decomposes at 75° . It is a strong acid, dissolves in alkalis, and expels carbonic anhydride from aqueous sodium carbonate when heated. Warm acids decompose it with formation of nitrosobenzene, but it is very stable in alkaline solution, even on boiling. Under the same conditions, finely-divided metallic iron also acts on nitrobenzene as a powerful reducing agent, but the final product of the reaction is aniline. The author considers that in the technical reduction of nitrobenzene the function of the hydrochloric acid is to produce a certain amount of ferrous chloride, which then acts in a similar manner to the calcium chloride employed in his experiments.

A. H.

Nitrites of certain Amines. By W. A. NOYES and H. H. BALLARD (*Ber.*, 27, 1449—1451).—Hexamethylenediamine nitrite is decomposed, by prolonged boiling in aqueous solution, into Δ^3 -tetrahydroaniline, 1:4-amidohydroxyhexamethylene, and dihydrobenzene; the last was recognised by its smell and the characteristic coloration with sulphuric acid and alcohol. Δ^3 -Tetrahydroaniline platinochloride crystallises from alcohol in yellow plates melting at 210° with decomposition. 1:4-Amidohydroxyhexamethylene platinochloride crystallises in flat, lemon-coloured plates, and is converted into the preceding compound by heating at 135° . Δ^3 -Tetrahydroaniline nitrite is more stable than hexamethylenediamine nitrite; after boiling for 25 minutes, only 16 per cent. was decomposed. β -Tetrahydronaphthylamine is the analogue of Δ^3 -tetrahydroaniline; the nitrite melts at 137° , and slowly decomposes on boiling; the chloride melts at 242 – 243° ; the nitrate at 215° . Bamberger and Lodter state (*Ber.*, 21, 854) that the nitrite is stable towards boiling water; their substance (m. p. 160°) is proved to be a mixture of nitrite and nitrate; they also give the melting point of the chloride as 237° . 2:5-Diamidohexane nitrite undergoes rapid decomposition on heating in aqueous solution. The authors point out that these observations tell against the "centric" benzene formula. J. B. T.

Stereoisomeric Anil-compounds. By W. v. MILLER and J. PLÖCHL (*Ber.*, 27, 1296—1304).—In the preparation of ethylden-aniline by shaking a mixture of aniline, acetaldehyde, and water, the chief product is the ethylden-aniline melting at 126° , but a small quantity of an isomeric compound melting at 85.5° is obtained. The two isomerides are separated by means of cold alcohol in which the base melting at 85.5° is soluble. The new base crystallises in long, thin, lustrous needles, has the same molecular weight as the ordinary modification, and, with nitrous acid, yields a nitroso-compound. When heated at 100° , it remains unaltered; at 120 – 130° , it is converted into the isomeride melting at 126° , and at 195° it is mostly converted into quinaldine-derivatives. It is most easily converted into the high melting modification by adding a small quantity of iodine to the ethereal solution and allowing the mixture to remain, or warming on the water bath. The same conversion takes place when the ethereal solution is treated with hydrogen chloride at 0° . When treated with benzoic chloride, it yields a small quantity of benzanilide, the benzoyl-compound of the high melting base which melts at 218° , and the benzoyl-compound of the new base which melts at 156° and crystallises in beautiful, rectangular tablets. When treated with acetic anhydride, it yields an acetyl-derivative which is an amorphous, yellow powder, whereas the ordinary modification (m. p. 126°) yields an acetyl-derivative which crystallises in beautiful needles and melts at 188° . When aniline hydrochloride and acetaldehyde react with one another in aqueous solution, the product consists of two-thirds ethylden-aniline (m. p. 126°) and one-third of the new modification. The best method of preparing the new modification is from aniline acetate and acetaldehyde in aqueous solution. Aniline sulphate and acetaldehyde yield only a small quantity of the new base.

E. C. R.

Derivatives of α -Diphenylsemicarbazide and of α -Diphenylthiosemicarbazide. By T. VAHLE (*Ber.*, 27, 1513—1519).—Phenylthiocarbimide unites directly with phenylhydrazones and with acid phenylhydrazides to form compounds which are probably derivatives of α -diphenylthiosemicarbazide, $\text{NHPh}\cdot\text{CS}\cdot\text{NPh}\cdot\text{NH}_2$, which is, itself, unknown. Analogous compounds are formed by phenylcarbimide and the acid phenylhydrazides.

Benzylidenediphenylthiosemicarbazide,



forms faintly yellow-coloured needles, melts at 182° , and is insoluble in hydrochloric acid and dilute soda. It only reduces Fehling's solution after vigorous boiling.

The corresponding *acetone*-derivative, $\text{NHPh}\cdot\text{CS}\cdot\text{NPh}\cdot\text{N}:\text{CHMe}_2$, forms thick, white needles, melts at 160° , and is soluble in warm hydrochloric acid. It does not act on Fehling's solution even when boiled with it.

Acetyl- α -diphenylsemicarbazide, $\text{NHAc}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NHPh}$, is obtained by heating acetylphenylhydrazine with phenylcarbimide. It forms small, white needles melting at 175 — 176° , and reduces Fehling's solution on boiling. An isomeric compound, melting at 183° , which is probably *acetyl- β -diphenylsemicarbazide*, $\text{NPhAc}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, is formed when diphenylsemicarbazide is treated with acetic anhydride.

Acetyl- α -diphenylthiosemicarbazide, $\text{NHAc}\cdot\text{NPh}\cdot\text{CS}\cdot\text{NHPh}$, forms very pale yellow needles melting at 131 — 132° .

Formyl- α -diphenylsemicarbazide, $\text{NHPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{COH}$, closely resembles the acetyl-compound, and melts at 171 — 172° . The corresponding *thio-compound* crystallises in white needles melting at 128 — 129° .

Butyryl- α -diphenylsemicarbazide forms small needles melting at 155° , whilst the corresponding *thio-compound* melts at 117 — 118° . Butyrylphenylhydrazide may be most conveniently prepared by adding butyric chloride to a dilute ethereal solution of phenylhydrazine (2 mols.); phenylhydrazine hydrochloride is precipitated, and the solution of the hydrazide may then be evaporated. The compound melts at 103 — 104° (stated as 113 — 114° by Michaelis and Schmidt, *Annalen*, 252, 308).

Benzoyl- α -diphenylsemicarbazide forms slender needles melting at 156° .

Phenylacetyl- α -diphenylsemicarbazide,



melts at 144° , whilst the *thio-compound* melts at 125 — 126° .

Cinnamyl- α -diphenylsemicarbazide forms small needles melting at 218 — 219° .

The acetyl-derivative of benzylphenylhydrazine, a secondary hydrazine, reacts in a similar manner with phenylcarbimide, *acetylbenzyl-diphenylsemicarbazide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NAc}\cdot\text{NPh}\cdot\text{C}_6\text{H}_5$, which melts at 145° , being formed.

The hydrazides of bibasic acids do not appear to react with phenylcarbimide or thiocarbimide.

A. H.

2 g 2

Diazobenzene Perbromide. By E. BAMBERGER (*Ber.*, **27**, 1273—1278).—Diazobenzene perbromide, when shaken with an aqueous solution of sodium hydroxide cooled with ice, yields nitrobenzene, benzenediazoic acid, and small quantities of azobenzene, benzoquinone, orthonitraniline, diphenyl, and carbylamine, together with some quantity of resinous products. The formation of nitrosobenzene from the perbromide is in accordance with its properties as tribromophenylhydrazine, which, when treated with alkalis, should yield nitrosophenylhydroxylamine, and then the latter decomposes according to the equation $\text{OH}\cdot\text{NPh}\cdot\text{NO} = \text{PhNO} + \text{NOH}$. The greater portion of the nitrosophenylhydroxylamine, however, undergoes molecular change with the formation of benzenediazoic acid. The production of nitrosobenzene is not due to the oxidation of diazobenzene by hypobromite, for only a very minute quantity of nitrosobenzene is formed when an acid diazochloride solution is added to an alkaline bromine solution.

The nitrosobenzene is obtained from the product of the reaction by extraction with ether. The ethereal solution also contains azobenzene, benzoquinone, and very small quantities of nitrobenzene, carbylamine, and diphenyl.

The alkaline liquid, after extraction with ether, contains benzenediazoic acid, orthonitraniline, and probably a salt of nitrosophenylhydroxylamine, since the barium salt, prepared by adding barium chloride to the neutralised solution, when treated with sulphuric acid, yields a small quantity of nitrosobenzene as well as benzenediazoic acid.

E. C. R.

Phenylhydroxylamine. By E. BAMBERGER (*Ber.*, **27**, 1548—1557).—The preparation of β -phenylhydroxylamine (this vol., i, 373, 409) from nitrobenzene is a matter of difficulty, since the experimental conditions cause the yield to vary from 0 to 57 per cent.; the physical state of the zinc-dust is of primary importance, and in order to obtain good results it is necessary to test each sample before use, and to modify the conditions accordingly. Phenylhydroxylamine is rapidly oxidised to azoxybenzene on exposure to air, but may be kept for an unlimited time in dry, air-tight vessels; on heating at 100° , it is resolved into azobenzene, aniline, azoxybenzene, paramidophenol, and small quantities of other substances; boiling with water causes a similar decomposition, nitrosobenzene being also formed. Alkalis convert phenylhydroxylamine immediately into nitrobenzene, which then gradually changes into azoxybenzene. The *hydrochloride*, $\text{NHPh}\cdot\text{OH}, \text{HCl}$, is colourless and crystalline.

The *benzylidene-derivative*, $\text{CHPh} < \begin{smallmatrix} \text{O} \\ \text{NPh} \end{smallmatrix}$, crystallises in lustrous, highly refractive prisms, melts at $108.5\text{--}109^\circ$, reduces alkaline copper solution on heating, and is resolved into benzaldehyde and paramidophenol (see below) by the action of mineral acids.

Phenylhydroxylamine is readily converted into paramidophenol on treatment with acids, quantities of azobenzene, and other substances, varying according to the experimental conditions, are simultaneously produced.

By the action of nitrous acid on phenylhydroxylamine, the *nitrosamine*, $\text{NO}\cdot\text{NPh}\cdot\text{OH}$, is formed, and crystallises from light petroleum in long, flat, lustrous needles melting at $58.5-59^\circ$; it gives Liebermann's reaction, and although certain specimens were stable, others decomposed spontaneously; the cause of this has not yet been determined. The yield is 85—90 per cent. of the theoretical. Nitrosophenylhydroxylamine is immediately converted into nitrosobenzene on heating with acids or water; with acids at ordinary temperatures, a diazo-compound is formed in addition. The nitrosamine reduces alkaline silver solution with difficulty, and alkaline copper solution not at all. The author's previous suggestion that the formation of nitrosobenzene from diazobenzene perbromide is preceded by that of nitrosophenylhydroxylamine (preceding abstract) is confirmed. The *potassium salt*, $\text{NO}\cdot\text{NPh}\cdot\text{OK}$, crystallises in lustrous plates, resembling naphthalene, and explodes on heating. The *sodium* and *barium salts* are crystalline. The *silver*, *copper*, *mercuric*, and *lead salts* are sparingly soluble. Nitrosobenzene is formed by the oxidation of phenylhydroxylamine; with potassium dichromate and sulphuric acid the yield is 90 per cent. of the theoretical. J. B. T.

Hydrogen Cyanide a Reagent for Symmetrical Oximes, Hydrazones, and Anil-compounds. By W. v. MILLER, J. PLÖCHL, and others (*Ber.*, 27, 1281—1296).—The authors have already shown that oximes and hydrazones with fatty alkyl-groups take up the elements of hydrogen cyanide, but that those with aromatic groups do not, whereas anil-compounds, both of the fatty and aromatic series, form additive compounds with hydrogen cyanide (*Abstr.*, 1892, 1189). The only exception to this is found in the behaviour of the anhydro compounds of pyruvic acid with amimes, for instance, $\text{NPh}\cdot\text{CMe}\cdot\text{COOH}$, &c. The authors have now arrived at the following conclusions:—1. All compounds of the type $\text{R}\cdot\text{C}\cdot\text{N}\cdot\text{R}'$ which combine with hydrogen cyanide are symmetrical as regards the nitrogen action, that is, the three bonds of the nitrogen lie in one plane, and stereoisomerides do not exist. 2. If, of two isomeric compounds of the above type, one combines with hydrogen cyanide, then the other is not a stereoisomeride, but either a structural isomeride or a polymeride. 3. All simple molecular compounds which do not combine with hydrogen cyanide contain asymmetrical nitrogen. The asymmetry of anil-compounds is determined by the distinct acid or basic properties of the radicle combined with the typical carbon atom, as for example in the anilide of pyruvic acid.

The anilides and toluidides of the glucoses, like other anilides, combine with hydrogen cyanide, and are converted into stable nitriles, they must, therefore, have the following constitution, glucose anilide and galactose anilide, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]\cdot\text{CH}\cdot\text{NPh}$, levulose anilide, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]\cdot\text{C}(\text{NPh})\cdot\text{CH}_2\cdot\text{OH}$. The nitriles are obtained by allowing the anilides to remain for some time with dilute hydrocyanic acid at the ordinary temperature, or by heating the anilides with aqueous hydrocyanic acid in a sealed tube at 40° . The nitriles decompose when heated above the melting point with evolution of

hydrogen cyanide, and when warmed with alkalis or water evolve an odour of isonitriles.

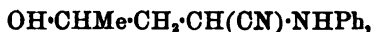
Anilidoglucose cyanide crystallises in bunches of needles, and melts at 166—168°; *toluidoglucose cyanide* melts at 128°; *anilidogalactose cyanide* melts at 138°; *toluidogalactose cyanide* melts at 145—146°; *anilidolevulose cyanide* melts at 131°.

When the above nitriles are allowed to remain for some time with fuming hydrochloric acid, they yield strongly acid, syrupy compounds which reduce silver and copper solutions. Crystalline phenylhydrazides are obtained when the nitriles are hydrolysed by allowing them to remain with very dilute alkali, and, after acidifying the solution with acetic acid, warming with phenylhydrazine. The hydrazides, when treated with concentrated sulphuric acid and ferric chloride, give a reddish-violet coloration.

Anilidoglucosecarboxylic acid phenylhydrazide crystallises in long interlacing needles, and melts at 210°; *toluidoglucosecarboxylic acid phenylhydrazide* crystallises in plates, and melts at 211—212°; *anilidogalactosecarboxylic acid phenylhydrazide* melts at 203°; *toluidogalactosecarboxylic acid phenylhydrazide* melts at 206°.

Glucoseoxime does not combine with hydrogen cyanide either at the ordinary temperature or when warmed at 40°. The hydrazone and osazone also do not combine with hydrogen cyanide.

Aldoleanilide, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NPh}$, is obtained by adding aniline to aldole in ethereal solution. It melts at 73—75°. The nitrile is best prepared by adding an ethereal solution of aldole to a mixture of aniline and hydrogen cyanide dissolved in ether. The product, *α -phenylamido- γ -hydroxyvaleronitrile*,



is a viscid, greenish-yellow oil. When hydrolysed with hydrochloric acid, it yields the lactone, $\text{NPh}\cdot\text{CH}\langle\begin{smallmatrix} \text{COO} \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CHMe}$, which crystallises in needles, and melts and decomposes at 59°. *α -Phenylamido- γ -hydroxyvaleric acid* is obtained by treating the lactone with sodium hydroxide; it crystallises in small nodules, and melts and decomposes at 143°.

The phenylhydrazide of aldole is prepared in a similar way to the anilide; it is a reddish oil. The nitrile is a viscid, greenish oil, which, when rubbed with concentrated hydrochloric acid, yields the lactone, $\text{N}_2\text{H}_2\text{Ph}\cdot\text{CH}\langle\begin{smallmatrix} \text{COO} \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CHMe}$, which crystallises in lustrous leaflets, and melts at 113°.

E. C. R.

Salts of Phenylhydrazine. By H. J. F. DE VRIES (*Ber.*, 27, 1521—1522).—*Phenylhydrazine formate* is a colourless, crystalline mass, which becomes yellowish-brown in the air; it is very readily soluble in water, and melts at 89—90°. *Phenylhydrazine lactate* melts at 102—103°. Formylphenylhydrazine, which is obtained instead of phenylhydrazine formate when an excess of formic acid is mixed with phenylhydrazine, melts at 140°, and not at 145°, as stated by other investigators.

A. H.

Dihydroxamic acids. By W. LOSSEN (*Ber.*, 27, 1481).—The action of alkalis on dihydroxamic acids, which Hantzsch (this vol., i, 364) thinks he has studied for the first time in the case of benz-acethydroxamic acid, was described long ago by the author.

C. F. B.

Nitrogen Halogen Compounds. By F. LENGFELD and J. STIEGLITZ (*Amer. Chem. J.*, 16, 370—372; compare *Abstr.*, 1893, i, 310, 631).—*Methylic paranitrophenylcarbamate*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COOMe}$, results, together with paranitraniline, from the reaction between paranitrobenzobromamide and sodium methoxide. It forms light, yellow crystals, melts at 176° , and volatilises when carefully heated, otherwise it explodes. It is identical with the carbamate synthesised from paranitraniline and methylic chlorocarbonate. The paranitraniline obtained as a co-product in the first process obviously results from the decomposition of the carbamate.

Methylic methylicarbamate, $\text{NHMe}\cdot\text{COOMe}$, results in a similar manner from the reaction between acetobromamide and sodium methoxide, and is also identical with the synthetical product. It is a colourless oil of peculiar odour, and boils at $55\text{--}60^\circ$ under a pressure of 25 mm., and at 158° under the ordinary pressure.

Jx. W.

Blue Lakes derived from Dibromogallanilide; Blue Reactions of Polyphenols. By P. CAZENEUVE (*Compt. rend.*, 118, 1046—1048).—When ammonia, or potassium or sodium hydroxide, is added carefully to a solution of dibromogallanilide, a deep indigo-blue compound is formed which is readily decomposed by excess of air or an excess of alkali. The blue colour becomes green, and then yellow. Under the same conditions calcium or barium hydroxide yields a white precipitate, which becomes blue on contact with air, the blue compound remaining unaltered when left in contact with water; a feeble acid, such as carbonic acid, decomposes the blue substance, and sets free a red acid which is decomposed by strong acids. The calcium and barium lakes alter in contact with air, but the zinc compound is more stable. It is prepared by adding zinc acetate solution to a dilute alcoholic solution of dibromogallanilide in the proportion of 2 mols. of the former to one of the latter, and is at first white, but becomes blue when exposed to air. The blue compound can be dried over sulphuric acid without undergoing appreciable alteration; it has the composition $\text{NHPh}\cdot\text{CO}\cdot\text{C}_6\text{Br}_2\text{O}_2(\text{O}_2\text{Zn})\cdot\text{OH}$.

It is noteworthy that all polyphenols derived from pyrogallol yield blue compounds. Gallic acid, dibromogallic acid, methylic dibromogallate, and the other ethereal salts, and the gallanilide, yield blue compounds which remain unaltered in contact with water for a long time. Purpurogallin and pyrogalloquinone yield fugitive blue compounds with ammonia.

C. H. B.

Iodoso- and Iodoxy-compounds. By C. WILLGERODT (*J. pr. Chem.*, [2], 49, 466—482).—In the first portion of this paper the author replies to the criticisms of V. Meyer (*Abstr.*, 1893, i, 713).

By chlorinating orthiodobenzoic acid in chloroform, yellow prisms, which melt and decompose at $115\text{--}123^\circ$, and are unstable in

air, are obtained. The composition of this compound agrees with the formula $C_6H_4<\overset{CO}{I}Cl>O$. When the chlorination is conducted in glacial acetic acid, a different chlorine derivative is obtained; this melts and partially decomposes at 95°. Iodosobenzoic acid (ortho-hydroxyiodobenzoate) has been prepared from the first-mentioned chloride by Meyer (Abstr., 1893, i, 507); by passing hydrogen chloride through a glacial acetic acid solution of the acid, prisms are formed which are apparently identical with the second chloride referred to above; they melt and decompose at 85–90°; water decomposes them with formation of iodosobenzoic acid. The nitrate, $C_6H_4<\overset{CO}{I}(NO_3)>O$, was prepared by heating a glacial acetic acid solution of iodosobenzoic acid with fuming nitric acid; it is decomposed by water into nitric acid and iodosobenzoic acid.

A. G. B.

Preparation of the Peroxides of the Acid Radicles. By H. v. PECHMANN and L. VANINO (*Ber.*, 27, 1510–1512).—Benzoic peroxide can be readily prepared by shaking a 10 per cent. solution of hydrogen peroxide with aqueous soda and benzoic chloride, a yield of 70 per cent. being obtained. This modified method may also be applied to the preparation of the peroxides derived from the bibasic acid which Brodie was unable to obtain, but the yields are not so satisfactory.

Phthalic peroxide, $C_8H_4O_4$, is best prepared by shaking a solution of sodium peroxide in aqueous sodium acetate with phthalic chloride. It is a crystalline powder, insoluble in the ordinary solvents. It melts when carefully heated at 133.5°, but explodes when rapidly heated or when struck. The substance may be analysed by heating it with a standard solution of stannous chloride. It possesses all the characteristic properties of the acid peroxides, liberates iodine from potassium iodide, decolorises indigo, &c.

A. H.

Bismuth Salts. By B. FISCHER and B. GRÜTZNER (*Arch. Pharm.*, 231, 680–686).—After reviewing the past work on “bismuthum salicylicum,” all of which shows the variability of the commercial product, the authors recommend the following method of obtaining a basic bismuth salicylate of constant composition, namely $BiO \cdot C_7H_5O_3$. Crystallised bismuth nitrate is dissolved in about four times its weight of dilute acetic acid (concentration not stated), the solution is diluted with about 40 times its weight of water, and the bismuth precipitated as hydroxide by the addition of ammonia. The precipitate is washed and mixed with a molecular proportion of salicylic acid. After a heating of some duration on the water bath, a magma of crystals of basic bismuth salicylate is formed. This is drained and dried, first on a porous tile and then in the air bath at 70–75°. The preparation is a dry, electrical, white powder, consisting of microscopic prisms, reddening moistened blue litmus only after a time. No salicylic acid can be detected in cold water in which the powder has been shaken.

Bismuth subgallate (dermatol), $C_6H_2(OH)_3 \cdot COO \cdot Bi(OH)_3$, may be prepared by a similar method from bismuth hydroxide and gallic acid. It is a sulphur-yellow powder, which does not part with gallic acid either to alcohol or to hot water.

A. G. B.

Methylic Parahydroxybenzoate. By C. H. v. HOESSLE (*J. pr. Chem.*, [2], 49, 501—502).—Ladenburg and Fitz prepared this compound, but they were dealing with an impure product when they determined its constants (*Annalen*, 141, 250). It crystallises in monoclinic, stellate needles, melts at 131° , and boils at 270 — 280° . Its *acetyl*-derivative crystallises in slender, felted needles, dissolves in alcohol, and melts at 85° . The *benzoyl*-derivative crystallises in slender, white needles, and melts at 135° ; it dissolves in hot alcohol, but not in water.

A. G. B.

Reduction Product of Orthosulphobenzoic Chloride. By W. JONES (*Amer. Chem. J.*, 16, 366—369).—Orthosulphobenzoic chloride is reduced by aqueous potassium hydrosulphide, with development of much heat, to the corresponding sulphonephthalide. This separates when the well-diluted product is acidified with hydrochloric acid. The same compound is obtained when zinc and dilute hydrochloric acid are substituted for the hydrosulphide. The product is dissolved in dilute caustic alkali, and isolated as before.

Sulphonephthalide, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{SO}_2 \end{smallmatrix} > O$, forms colourless crystals, and melts and decomposes at 287 — 289° . It reduces permanganate, and is oxidised by concentrated nitric acid to orthosulphobenzoic acid. It forms a fluorescent compound with resorcinol, but oxidation probably occurs at an intermediate stage. The constitution of the phthalide is probably that represented by the above formula, but is still under investigation.

JN. W.

Indoxazenes. By A. HEIDENREICH (*Ber.*, 27, 1452—1456; compare Cathcart and V. Meyer, *Abstr.*, 1893, i, 94).—*Orthobromophenyltolyl ketone* is prepared by the action of aluminium chloride on orthobromobenzoic chloride and toluene, and crystallises from alcohol in long needles melting at 92 — 93° . The *oxime* is crystalline, and melts

at 138 — 140° . *Tolylindoxazene*, $C_6H_4 \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \cdot N \geq C \cdot C_6H_4Me$, is formed by heating the preceding compound with aqueous alkali or sodium ethoxide, and crystallises in long, colourless needles; it boils at 344 — 346° , and melts at 81 — 82° . The *dinitro*-derivative is crystalline, and melts at 187 — 188° . *Dibromobenzophenone*, prepared from orthobromobenzoic chloride, bromobenzene, and aluminium chloride, crystallises from alcohol, and melts at 51 — 52° . The *oxime* is crystalline, and melts at

140 — 142° . *Parabromophenylindoxazene*, $C_6H_4 \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \cdot N \geq C \cdot C_6H_4Br$, crystallises in long needles, and melts at 132 — 133° . *Ethoxyorthobromobenzophenone* is prepared in a similar manner to the preceding ketones, and forms greenish crystals melting at 79° . The *oxime* melts at

161—163°. *Ethoxyphenylindoxazene*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{O} \cdot \text{N} \end{smallmatrix} \gg \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$, is deposited from alcohol in brownish crystals melting at 59—61°. *Methoxyorthobromobenzophenone* is colourless and crystalline, and melts at 95—95.5°. The *oxime* could not be obtained in a state of purity. *Methoxyphenylindoxazene*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{O} \cdot \text{N} \end{smallmatrix} \gg \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, is deposited from alcohol in slender, lustrous crystals melting at 100—101°. Attempts to extend this reaction to the thiophen and naphthalene series were unsuccessful, it was not even possible to prepare the corresponding ketones.

J. B. T.

Benzidinetiethiocarbimides. By M. JAFFÉ (*Ber.*, 27, 1557—1561).—*Diphenylenedithiocarbimide*, $\text{C}_{12}\text{H}_8(\text{NCS})_2$, is prepared by the interaction of benzidine and thiocarbonyl chloride at 180°, and crystallises from benzene in highly refractive, colourless needles melting at 203°. By the action of ammonia, two compounds are formed, the one, $\text{NH} < \begin{smallmatrix} \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \\ \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \end{smallmatrix}$, crystallises from benzene in lustrous plates, which remain unmelted at 300°; the second is *diphenylenedithiocarbamide*, $\text{C}_{12}\text{H}_8(\text{NH} \cdot \text{CS} \cdot \text{NH}_2)_2$; this is obtained pure by the action of alcoholic ammonia on the imide, and is only soluble in nitrobenzene. *Diphenylenediisopropylthiocarbamide* is prepared by heating benzidinetiethiocarbimide and isopropylamine in benzene solution; it is a colourless, amorphous powder, which is unmelted at 300°; a second modification, crystallising in needles, is deposited from the mother liquor, and melts at 170°. *Diphenylenediamyldithiocarbamide* is prepared in a similar manner to the preceding compound, which it closely resembles, the mother liquor on standing deposits *diphenyleneamyldithiocarbamide*, $\text{C}_8\text{H}_{11} \cdot \text{N} < \begin{smallmatrix} \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \\ \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \end{smallmatrix}$, which is crystalline, and melts at about 148°.

Diphenylenediorthotolylthiocarbamide, prepared from orthotoluidine and benzidinetiethiocarbimide is amorphous, is not melted at 300°, and on repeatedly heating in benzene solution becomes insoluble. *Diphenylenediphenyldithiocarbamide* is already known, and, like the preceding compound, exists in a colloidal form; by the action of phenylhydrazine the *thiosemicarbazide*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CS} \cdot \text{NPh} \\ \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \end{smallmatrix}$, together with the *disemicarbazide*, $\text{C}_{22}\text{H}_{24}\text{N}_4\text{S}_2$, are formed; the former crystallises from benzene in thin plates, and melts and decomposes at 220—230°, the latter is amorphous, insoluble, and does not melt. *Unsymmetrical diphenylenetetraisobutylthiocarbamide*, $\text{C}_{18}\text{H}_{26}[\text{NH} \cdot \text{CS} \cdot \text{N}(\text{C}_4\text{H}_9)_2]_2$, from benzidinetiethiocarbamide and diisobutylamine, crystallises from alcohol in colourless needles melting at 185°. The corresponding *amyl derivative* crystallises in needles melting at 162°. A second modification melting at 123° was also obtained. *Diphenylenedimethyldiphenyldithiocarbamide*, from the thiocarbamide and methylaniline, is crystalline. *Diphenylenedipiperidyldithiocarbamide* crystallises from alcohol in slender, colourless needles, melts at 214—215°, and by prolonged heat-

ing with benzene is converted into an insoluble modification, which does not melt.

J. B. T.

Tetramethyldiamidobenzhydrol. By H. WEIL (*Ber.*, **27**, 1403—1409).—The reactions described below resemble those of ketones and aldehydes, and lead to the conclusion that tetramethyldiamidobenzhydrol has not the constitution $\text{OH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, but $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, or, possibly,

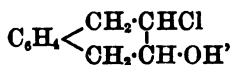


in which one of the benzene rings is dihydrogenised. In the case of the action of sodium hydrogen sulphite or of hydrogen cyanide the CO group may be supposed to first react as usual, an interchange of OH and H then taking place, with subsequent loss of H_2O and formation of the substance actually obtained.

Tetramethyldiamidobenzhydrol yields with hydroxylamine the *oxime*, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, melting and decomposing at 154° . With sodium hydrogen sulphite it yields the sodium salt of a *sulphonic acid*, $\text{SO}_3\text{H}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, which, when heated, evolves sulphurous anhydride at 120 — 130° ; the acid can also be obtained by the action of sulphurous anhydride on the hydrol in alcoholic solution. With hydrogen cyanide, it yields a *nitrile*, $\text{CN}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, which melts at 124° , and behaves like a leucobase, being capable of oxidation to a green-colouring matter. The nitrile can be converted by hydrolysis into a *carboxylic acid*, $\text{COOH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, which greatly resembles the sulphonic acid in physical properties. When the hydrol is boiled with a concentrated solution of ammonium acetate carefully kept feebly alkaline with ammonia, a compound $\text{NH}[\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2]_2$, melting at 185° , is formed.

C. F. B.

Ketotetrahydronaphthalene. By E. BAMBERGER and A. VOSS (*Ber.*, **27**, 1547—1548).—The preparation of ketotetrahydronaphthalene, $\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix}$, from tetrahydronaphthalene chlorhydrin,



by distillation with magnesium carbonate or quinoline has been previously described (*Abstr.*, 1893, 1591). The yield is small. The ketone is a colourless, highly refractive oil, which solidifies in a freezing mixture, melts at 18° , and boils at 138° under 16 mm. pressure; under ordinary pressure, the boiling point is 130 — 140° , and a portion is decomposed into naphthalene and water. The sodium hydrogen sulphite derivative crystallises in colourless,

lustrous plates. The *phenylhydrazone*, $\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{C}\cdot\text{N}_2\cdot\text{HPh} \end{smallmatrix}$, is deposited in colourless, lustrous crystals which melt at 107.5 — 108° ; it rapidly decomposes on exposure to sunlight, and gives Bulow's re-

action. The *oxime*, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot C \cdot NOH \end{smallmatrix}$, crystallises from dilute alcohol in silky, lustrous, stellate needles melting at $87.5-88^\circ$.

J. B. T.

Derivatives of Naphthyl Ethyl Ether. By P. HEERMANN (*J. pr. Chem.* [2], **49**, 504).—A reply to Duisberg (this vol., i, 336).

β -Anthraquinone. By K. LAGODZINSKI (*Ber.*, **27**, 1438—1439).—When 2-hydroxyanthracene is heated in alcoholic solution with sodium nitrite and zinc chloride, it is converted into a salt of *nitroso-hydroxyanthracene*, which in the free state forms a brown mass. On treatment with stannous chloride and hydrochloric acid this is reduced to *amidohydroxyanthracene*, the hydrochloride of which crystallises in slender, matted needles, which do not change in the air. When this substance is oxidised by means of chromic acid, a new anthraquinone is formed which crystallises from a mixture of benzene and light petroleum in beautiful, orange-yellow needles, and is almost insoluble in water. It melts and decomposes at about 180° . With phenylenediamine it reacts with great readiness, forming an azine, which exhibits the usual reactions with acids. It has not yet been determined whether the compound is a 1:2- or a 2:3-quinone.

A. H.

Truxene. By C. LIEBERMANN (*Ber.*, **27**, 1416—1418).—A polemical paper in relation to the author's work (with Bergami) (*Ber.*, **22**, 752; **23**, 317) and that of Kipping (*Proc.*, 1892, 107; *Trans.*, 1894, 269).

The Truxillic acids. By H. LANGE (*Ber.*, **27**, 1410—1415).— γ -Truxillic acid yields derivatives with toluidine which are analogous to those obtained with aniline (*Abstr.*, 1893, i, 418). γ -*Truxillotoluidic acid*, $HOOC \cdot C_{10}H_{14} \cdot CO \cdot NH \cdot C_6H_4Me$, forms white, needle-shaped crystals, melts at 268° , and is less soluble in aqueous soda than γ -truxillic acid itself. The *barium* salt is sparingly soluble in water. γ -*Truxilloditoluidide*, $C_{10}H_{14}(CO \cdot NH \cdot C_6H_4Me)_2$, is obtained by the use of an excess of toluidine, and melts at 289° .

All the three isomeric truxillic acids react with phenylhydrazine to form hydrazides. The α -acid only forms one compound, α -*truxillodiphenylhydrazide*, $C_{10}H_{14}(CO \cdot NH \cdot NPh)_2$, which is insoluble in the usual reagents and in alkalis, but crystallises from phenol or acetin in white needles melting at 320° .

γ -*Truxillodiphenylhydrazide* is a similar substance, and melts at 305° . When truxillic anhydride is heated with phenylhydrazine, however, γ -*truxillophenylhydrazide*, $C_{10}H_{14}(CO)_2N \cdot NPh$, is obtained. This compound is also sparingly soluble in most solvents, and separates from acetic acid in white prisms melting at 249° . It corresponds with the hydrazide obtained from the β -acid, and marks the distinction between these two and the α -acid, which is incapable of forming an anhydride. γ -Truxillic acid reacts with sulphuric acid in a different manner from the α - and β -acids (*Abstr.*, 1889, 698). No truxillodisulphonic acid or truxone is produced, but the acid is converted into *dicinnamenedisulphonic acid*, $C_{18}H_{14}(SO_3H)_2$.

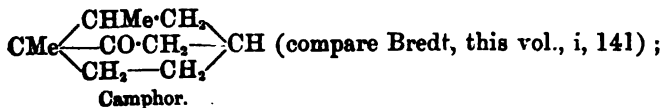
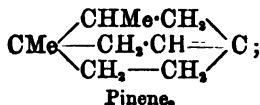
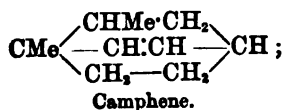
A number of acid salts of the α - and γ -acids have also been prepared, the bibasic character of these acids being thus further confirmed. *Hydrogen silver α -truxillate*, $\text{COOH}\cdot\text{C}_{10}\text{H}_{14}\cdot\text{COOAg}$, is almost insoluble in water, readily soluble in ammonia. *Hydrogen methylic α -truxillate* is prepared from the hydrogen silver salt. It forms small, white needles, and melts at 195° . *Silver methylic α -truxillate* is a white precipitate. *Hydrogen silver γ -truxillate* resembles the corresponding α -salt. The *hydrogen methylic* salt of the γ -acid melts at 180° , and the *silver methylic* salt is a white precipitate.

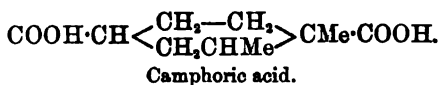
The γ -acid does not yield a fluorescein, and differs in this respect from the β -acid. A. H.

Oxidation Products of Carvole. By O. WALLACH (*Ber.*, 27, 1495—1496; compare *Abstr.*, 1893, i, 596). A paper has recently been published by Best (this vol., i, 361) dealing with the products of oxidation of carvole, which have previously been described by the author. These products are still under investigation. The acid of higher melting point when pure crystallises well, and melts at 192.5° (previously stated as 185°) with loss of water. It has the composition $\text{C}_8\text{H}_{10}\text{O}_2$, and yield a white *silver* salt, $\text{C}_8\text{H}_{11}\text{O}_2\text{Ag}$. When this acid is distilled under diminished pressure, it is converted into a neutral substance of the formula $\text{C}_8\text{H}_{10}\text{O}_4$ (previously stated to be $\text{C}_{10}\text{H}_{12}\text{O}_2$), melting at 129° . The acid described as melting at about 100° , crystallises well when pure, and melts at 94 — 95° . It is isomeric with terpenylic acid, $\text{C}_8\text{H}_{12}\text{O}_4$, is a well marked bibasic acid, and forms a *silver* salt, $\text{C}_8\text{H}_{10}\text{O}_4\text{Ag}_2$. A. H.

Stereoisomerism in the Camphor Group. By L. BOUVEAULT (*Bull. Soc. Chim.*, [3], 11, 134—144; compare *Abstr.*, 1893, i, 523).—The author has already described a saturated hydrocarbon isomeric with hydrocamphene, obtained by the action of sodium on boiling pinene hydrochloride (*loc. cit.*). In order to explain the relation between these two compounds, an hypothesis is developed embodying an application to the terpene series of v. Baeyer's views regarding the *cistrans*-isomerism of hexamethylene derivatives (compare A. v. Baeyer, this vol., i, 92). The liquid hydrocarbon is now called *cis-hydrocamphene*, the previously known, solid modification receiving the name *cistrans-hydrocamphene*. To these isomerides the author assigns

the constitution $\text{CMe} \begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2\text{—CH}_2 \end{array} \text{CH}$, thence deducing the following constitutional formula:





According to the views adopted by the author, camphoric acid could exist in four modifications; whilst camphor, camphene, hydrocamphene, and pinene hydrochloride might each be expected to occur in two stereoisomeric forms.

M. O. F.

Optical Isomerism of Closed Chain Compounds. By L. BOUVEAULT (*Bull. Soc. Chim.*, [3], 11, 144—147).—A further discussion of cistrans-isomerism in the terpene series.

M. O. F.

Bredt's Camphor Formula. By O. ASCHAN (*Ber.*, 27, 1439—1446).—The author considers Bredt's formula for camphor (this vol., i, 141) the best hitherto suggested, but it fails to explain the non-formation of an unsaturated acid or anhydride by the elimination of hydrogen bromide from bromocamphoric anhydride; that the bromine in this compound is linked to a tertiary carbon atom as in bromobenzene is irrelevant, since the anhydride does not contain a benzene linkage. The readiness with which hydrogen bromide is eliminated from the two α -bromohexahydrotetraphthalic acids, α -bromohexahydrobenzoic acid, α -bromohexahydroparatoluic acid, and from α -bromethylcyclopentanecarboxylic acid, would suggest that bromocamphoric anhydride, which, like this last acid, contains the group $\text{CH}_2\cdot\text{CBr}\cdot\text{CO}$, should behave in a similar manner. Since the bromine atom is readily eliminated, we must conclude that it is probably linked to a secondary carbon atom which is itself linked either to two tertiary carbon atoms, or to one of these and to a carboxyl group. Similar arguments are applied to bromocamphor; according to Bredt this contains the group $\text{CH}\cdot\text{CHBr}\cdot\text{CO}$, but in this case, too, hydrogen bromide is not eliminated, as from analogy would be expected; the compound remains unaltered by prolonged boiling with aniline or quinoline.

Bromocamphocarboxylic acid is readily prepared by the action of bromine on camphocarboxylic acid in glacial acetic acid solution, and melts at 112—113°; the substance obtained by Silva's method is impure, and melts at 109—110°. Bromocamphor was prepared from the preceding compound by the action of alcoholic potash at the ordinary temperature.

J. B. T.

Formation of Camphorquinone by the Oxidation of Camphocarboxylic acid with Potassium Permanganate. By O. ASCHAN (*Ber.*, 27, 1446—1449).—Bromocamphocarboxylic acid and camphocarboxylic acid are stable towards potassium permanganate in alkaline solution at ordinary temperatures; the former acid is only slowly decomposed on boiling, the latter, at 60—70°, yields camphorquinone, camphoric anhydride, and camphoric acid. The yield of quinone is 0.25 per cent. of the acid employed. The camphoric anhydride is almost certainly formed from the quinone, and the yield varies according to the experimental conditions. The preparation of

camphoric acid by the oxidation of camphor with nitric acid is probably preceded by the formation of camphorquinone and camphoric anhydride. These results are not in agreement with the camphor formulæ, which, like that of Collie (Abstr., 1892, 864), represent the production of camphoric acid from camphor as involving molecular rearrangement of the ring system.

J. B. T.

Galbanum Resin. By A. CONRADY (*Arch. Pharm.*, 232, 98—130).

—This substance has been submitted to a careful examination, and is found to consist of (1) an ethereal oil, 9·5 per cent.; (2) a resin soluble in alcohol, 63·5 per cent.; (3) impurities and gum, 27·0 per cent. The pure resin, obtained from the commercial product by extraction with alcohol and subsequent treatment with sodium salicylate, contains (1) combined umbelliferone, 20 per cent.; (2) galbaresinotannol, 50 per cent.; (3) free umbelliferone, 0·25 per cent. A solution of the pure resin in cold caustic potash shows a blue fluorescence, indicating the formation of umbelliferone; on heating the solution, umbellic acid is formed. Since umbelliferone is unattacked by sulphuric acid, the hydrolysis of the resin is best effected by that reagent, about 20 per cent. of umbelliferone being obtained in this way; the other product of hydrolysis is *galbaresinotannol*, $C_{18}H_{30}O_8$, from which *barium*, *acetyl*, and *benzoyl* derivatives were obtained, the two latter melting at 61° and 73° respectively. *Galbaresinotannol*, therefore, contains an hydroxyl group, and the pure resin is most probably a galbaresinotannyl salt of umbelliferone. Distillation of the resin alcohol with phosphoric anhydride gives rise to a hydrocarbon of the formula $C_{15}H_{20}$, and oxidation with nitric acid (sp. gr. = 1·27) leads to the formation of camphoric and camphoronic acids. The ethereal oil of commercial galbanum oil undergoes decomposition in a current of steam, with formation of isovaleric acid and a terpene, probably associated with a sesquiterpene (compare Wallach, Abstr., 1887, 596).

M. O. F.

Peru Balsam. By H. TROG (*Arch. Pharm.*, 232, 70—98).—By suitable treatment with carbon bisulphide, ether, and a dilute solution of caustic soda (0·5 per cent.), Peru balsam is divided into two constituents, an oil and a resin, both of which have been carefully examined.

The author summarises his results as follows. The liquid portion of Peru balsam, known as cinnamein to earlier investigators, consists chiefly of benzylic benzoate with a small quantity of benzylic cinnamate; ethylic and phenylpropylic cinnamates, benzylic alcohol, and benzoic acid were not detected, but cinnamic acid and vanillin are present in very small quantities. The resin, when hydrolysed, yields cinnamic acid and a small quantity of benzoic acid, together with *peruresinotannol*, a resin alcohol of the formula $C_{18}H_{30}O_6$, forming a pale brown, odourless powder, which shrinks and gradually decomposes when heated. From *peruresinotannol* were obtained a *potassium salt*, and *acetyl*, *benzoyl*, and *cinnamyl* derivatives. It can be brominated, and is oxidised by concentrated nitric acid to oxalic and picric acids (compare Lüdy, Abstr., 1893, i, 480).

The bark of *Myroxylon Pereirae* contains very small quantities of phloroglucinol, tannic acid, phlobaphen, and wax, together with an unsaponifiable resin, but it is free from all the constituents of the balsam. Since the uninjured bark contains neither secreting vessels nor secretions, Peru balsam must be regarded, similarly to gum benzoin, as a pathological product, its formation being probably due to an accumulation of tannin, caused by bruising the bark.

M. O. F.

Flores Koso. By M. LEICHSENING (*Arch. Pharm.*, 232, 50—65).—From this drug, the author has isolated two individual substances, in addition to kosin, which has hitherto been regarded as the principle to which the koso bloom owes its vermifugal action. Kosin, $C_{22}H_{30}O_7$ (compare Flückiger and Buri, this Journal, 1875, 468), crystallises from boiling alcohol in tufts of long, pale yellow needles, which melt at 148° . It is uncertain whether kosin contains hydroxyl groups, but, when it is heated at 150 — 170° with sulphuric acid in a closed tube, two molecular proportions of isobutyric acid are eliminated; if hydrochloric acid is employed, an amorphous, red substance is formed, very similar to that obtained in association with isobutyric acid by the decomposition of filicic and pannic acids. Kosin is almost insoluble in weak alkalis, and is non-poisonous.

Protokosin, $C_{22}H_{32}O_8$, is isolated from the ethereal extract of the drug in the form of long, colourless, shining needles, melting at 176° . It is insoluble in water, and but slightly soluble in cold alcohol, dissolving readily in ether; when heated alone or with sulphuric acid, an odour of isobutyric acid becomes perceptible. Protokosin is without physiological action, and the poisonous character of the original drug has now been traced to the presence of *kosotoxin*, $C_{22}H_{34}O_{10}$, a pale yellow powder, which melts at 80° . It is insoluble in water, but dissolves readily in alcohol, ether, aqueous alkalis, and alkali carbonates. It has no action on litmus, and closely resembles kosin in properties, giving rise to isobutyric acid when heated alone or with sulphuric acid. A solution of kosotoxin in potash reduces copper sulphate when boiled, an ammoniacal solution causing silver nitrate to deposit a metallic mirror. Ferric chloride develops, in an alcoholic solution, a deep, brownish-red coloration, this being immediately destroyed by hydrochloric acid. In distinction from kosin, kosotoxin yields two molecular proportions of isobutyric acid when heated with caustic potash, and, if boiled for 20 minutes with a 5 per cent. solution of barium hydroxide, gives rise to the formation of kosin.

M. O. F.

Pyridine Series. By S. RUHEMANN (*Ber.*, 27, 1266—1273; see also *Ber.*, 27, 1099).—*Phenylhydrazonoethylhydroxyfumaric acid*. $NHPh:C(COOH):C(COOH):C(OH)\cdot COOH$, is obtained by heating the hydrazone, $C_{12}H_{12}ClN_4O_2$, obtained from chlorodiketohydroxyisonicotinamide, with potassium hydroxide. It is separated by converting into the *silver salt*, $C_{12}H_{11}N_4O_7Ag_3$, and treating the latter with hydrogen sulphide. It crystallises in slender, yellow needles, and melts at 130° , gas being evolved. The *methylic salt* is obtained by warming the silver salt with methylic iodide, and, when treated with

concentrated ammonia, is converted into the *amide* of *phenylhydroxypyridazonedicarboxylic acid*, $\text{NPh} \cdot \text{N} = \text{C} \cdot \text{CONH}_2$, $\text{CO} \cdot \text{C}(\text{OH}) : \text{C} \cdot \text{CONH}_2$. This crystallises in colourless needles and melts at 237–238°.

When citrazinamide is heated with a solution of potassium hydroxide in a sealed tube at 150°, it is converted into aconitic acid (m. p. 187°). A decomposition analogous to that obtained by the action of potassium hydroxide on the pyridine compounds derived from citrazinamide.

The author has already described dihydroxypyridines derived from the ethereal salts of homologues of glutaconic acid (Trans., 1893, 874). These compounds give a yellow coloration with ferric chloride. The author has obtained, from their mother liquors, isomeric compounds, which yield a violet coloration with ferric chloride.

The compound, obtained by the action of ammonia on methylic glutaconate, which melts at 190–191°, yields a dibromo-derivative, which has the constitution $\text{CH} < \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{OH}) \\ \text{CBr}_2 \cdot \text{CO} \end{smallmatrix} > \text{N}$, and not that previously assigned to it, for, by the action of phenylhydrazine, it yields the *phenylhydrazone* of *methyl diketohydroxypyridine*, which crystallises in yellowish-red needles and decomposes at 240°.

Phenylmethylpyridazonedicarboxylic acid, $\text{CO} < \begin{smallmatrix} \text{NPh} \cdot \text{N} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} > \text{C} \cdot \text{COOH}$, is obtained by boiling the preceding hydrazone with potassium hydroxide in a reflux apparatus. It crystallises in colourless needles, melts at 216°, and is a strong acid. E. C. R.

Crystalline form of β -Pipicoline Tartrate. By A. LADENBURG (*Ber.*, 27, 1409–1410).—The data given in a previous communication (this vol., i, 208) apply to *dx*-pipicoline dextrotartrate. The corresponding data for *lβ*-pipicoline dextrotartrate are as follows. The crystals are strongly developed, parallel to the vertical axis, and belong to the hemihedral division of the rhombic system. Axial ratio = 0.28801 : 1 : 0.30255. A. H.

Derivatives of Picolinic acid and their Conversion into α -Amidopyridine. By H. MEYER (*Monatsh.*, 15, 164–182).—The ethylic salts of the pyridinemonocarboxylic acids cannot be prepared in the usual ways, betaines being formed instead. The author has now succeeded in preparing *ethylic picolinate* by heating an intimate mixture of dry potassium ethylic sulphate and potassium picolinate, moistened with absolute alcohol, for 7–9 hours at 150° in an autoclave. In this reaction, ethylpyridylum hydroxide is also produced. Ethylic picolinate forms a colourless oil of faint aldehydic odour and burning taste. It boils at 240–241° (corr.), and remains liquid at –17°, but at –65° solidifies to colourless crystals melting at 0–2°. It is volatile in steam, but at the same time undergoes slight hydrolysis. It is at once hydrolysed by cold, moist silver oxide; slowly by heating with hydrochloric acid, with formation of picolinic acid hydrochloride. It is also very slowly hydrolysed by boiling water. Mixed with concentrated hydrochloric acid and kept in a vacuum over lime,

ethylic picolinate hydrochloride is formed in deliquescent crystals, yielding an orange crystalline *platinochloride* melting with decomposition at 154° (uncorr.). When boiled with water, this *platinochloride* decomposes, picolinic acid *platinochloride* being formed. *Ethylic picolinate ethiodide* crystallises in lemon-yellow scales melting at $104\text{--}105^{\circ}$ (uncorr.), and is exceedingly soluble in water and alcohol, more sparingly in benzene and chloroform, and insoluble in ethylic iodide and in ether. The crystals belong to the rhombic system

$$[a : b : c = 0.7805 : 0.7737 : 1].$$

When treated with silver oxide, the ethiodide yields *picolinic acid ethylbetaine*, $C_7H_9N\text{EtO}_2$, crystallising in colourless plates or needles of bitter taste, and very soluble in water and alcohol. It gives no coloration with ferrous sulphate, and its salts are soluble in water. The *platinochloride*, $C_7H_9NO_2Cl.PtCl_4$, forms yellow scales melting with decomposition at 176° . When heated continuously at 100° , the betaine evolves carbonic anhydride, and forms ethylpyridylum hydroxide. When heated with alcoholic ammonia at $105\text{--}110^{\circ}$, ethylic picolinate yields *picolinamide*, which crystallises in colourless, monoclinic needles, $a : b : c = 1.5588 : 1.3423 : 1$. It melts at 103.5° , sublimes, distils undecomposed, and is volatile in steam. It is sparingly soluble in light petroleum, easily so in the other usual solvents. When treated with bromine and dilute potash, it yields α -amidopyridine (Markwald, Abstr., 1893, i, 737); this melts at 92° , boils at 200° (uncorr.) (Markwald gives 56° and 204° respectively), and crystallises in glistening scales. The *hydrochloride* forms colourless, prismatic tables deliquescent in air; the *platinochloride* small triclinic needles $[a : b : c = 1.1735 : 0.6572 : 1]$, and melts at $227\text{--}228^{\circ}$ (uncorr.). The yield of α -amidopyridine is, by this method, about 85 per cent. of the theoretical.

Ethylpyridylum hydroxide is also formed by acting on pyridine with potassium ethylic sulphate so that its formation as above may be from the previous formation of either the betaine or of pyridine. The *mercurichloride*, $C_7H_9NCl.HgCl_2$, crystallises in white needles melting at 111.5° , and volatilises without leaving a residue; the *aurochloride*, $C_7H_9NCl.AuCl_3$, forms yellow needles melting at 141° ; the *platinochloride* glistening rhombic plates

$$[a : b : c = 0.7080 : 0.7155 : 1],$$

melting at 193° . The author has prepared ethylpyridylum hydroxide by Anderson's method (*Annalen*, 94, 358), and compared it with that prepared as above.

When treated with sodium in alcoholic solution by Ladenburg's method, ethylic picolinate yields ethylic picecolinate; this forms deliquescent crystals, and gives a *platinochloride* melting at $110\text{--}112^{\circ}$.

Methylic picolinate is prepared in a similar way to the ethylic salt, but the heating must not be carried above $110\text{--}120^{\circ}$. It is a slightly yellow oil, of pleasant odour, boiling at $225\text{--}227^{\circ}$ (uncorr.). Its *amide* melts at $103\text{--}104^{\circ}$. Methylpyridylum hydroxide is also formed, but only in small quantity.

The alkyl salts of picolinic acid are also formed by distilling a

mixture of potassium alkyl sulphate and potassium picolinate, but the yield is small.
L. T. T.

Synthesis of Quinoline Derivatives. By S. NIEMENTOWSKI (*Ber.*, 27, 1394—1403).—When anthranilic acid is heated for two or three days with acetophenone at 120—130°, 2'-phenyl-4'-hydroxyquinoline is formed. From metahomoanthranilic acid and acetophenone, 2-methyl-2'-phenyl-4'-hydroxyquinoline is formed; it crystallises in long plates, melts at 270°, and has both acid and basic properties. When boiled with ethylic acetoacetate, anthranilic acid yields two condensation products, namely, 2'-methyl-4'-hydroxyquinoline-3'-carboxylic acid, and, in larger quantity, a substance, $C_{22}H_{16}N_2O_6$, which appears to be an anhydride derived from 2 mols. of the first substance. This anhydride melts at 335°, and yields a *disodium salt*, $(9H_2O)$; it is very stable to ordinary reagents, but, when distilled with zinc-dust, yields a mixture of quinoline and methylquinoline. Metahomoanthranilic acid yields with ethylic acetoacetate, in similar fashion, 2 : 2'-dimethyl-4'-hydroxyquinoline-3'-carboxylic acid, melting at 249°, and a substance, $C_{24}H_{20}N_2O_6$, melting above 350°. Ethylic ethylacetoacetate only forms the dimolecular compounds; with anthranilic acid, it yields a substance, $C_{26}H_{24}N_2O_6$, melting at 286°; with metahomoanthranilic acid, a substance, $C_{28}H_{26}N_2O_6$, melting above 345°. It will be noticed that all these substances which condense with anthranilic acid or its homologue contain the group $-CH_2CO-$. In no case is the yield very satisfactory.

C. F. B.

Hexahydroquinoline. By H. TRETZE (*Ber.*, 27, 1478—1481).—This substance, C_6NH_{12} (compare Bamberger and Lengfeld, *Abstr.*, 1890, 1318), resembles the tetrahydro- more than the decahydro-compound. It boils at 224·5—225° under 712 mm. pressure; its *sulphate* melts at 174°; its *hydrochloride* at 171°. With phenylthiocarbamide, it yields *hexahydroquinolylphenylthiocarbamide*, $C_6NH_{11}CS\cdot NPh$, melting at 127·5°; with phenylic cyanate, *hexahydroquinolylphenylcarbamide*, $C_6NH_{11}CO\cdot NPh$, melting at 159—161°; with carbon bisulphide, *dihexahydroquinolylthiocarbamide*, $CS(C_6NH_{11})_2$, melting at 129°; with potash and benzoic chloride, *benzoylhexahydroquinoline*, $C_6NH_{11}Bz$, melting at 119—121°. When oxidised with alkaline permanganate, it yields benzoylanthranilic acid, together with benzamide, and benzoic and oxalic acids. Hexahydroquinoline absorbs 2 atoms of bromine, but the product is readily decomposed by water; if the resulting oil is shaken out with ether, and the ethereal solution treated with hydrogen bromide, white crystals of *monobromohexahydroquinoline hydrobromide*, melting at 184°, are obtained.

C. F. B.

Decahydroquinoline. By E. BAMBERGER and S. WILLIAMSON (*Ber.*, 27, 1458—1478; compare *Abstr.*, 1890, 1318).—Tetrahydroquinoline was reduced, as before, by heating with phosphorus and hydriodic acid. The product of the reaction is distilled with steam, when propylhexamethylene and propylbenzene distil over, together with an iodoquinoline derivative (probably diiododecahydroquinoline) that yields hexahydroquinoline when boiled with alcoholic potash.

Soda is added to the residue, and the distillation continued; decahydroquinoline now distils over, accompanied by hexahydroquinoline, which may be removed by shaking out the ethereal solution of the mixed bases with very dilute acetic acid.

Decahydroquinoline *picrate*, $C_9NH_{17}C_6H_2N_3O_7$, softens at 146° , and melts at $151-152^\circ$. The *chlorimide*, $C_9H_{16}NCl$, obtained by treating the base with bleaching powder solution, melts at 125.5° . The base itself, when treated with methylic iodide in ethereal solution, yields *dimethyldecahydroquinolinium iodide*; the *platinochloride*,



forms orange-red prisms melting with decomposition at 247° . When boiled for a long time with aqueous potassium methylic sulphate, it yields *methyldecahydroquinoline*, $C_9NH_{16}Me$, as a colourless, mobile oil, which boils at $204.5-205.5^\circ$, under 721 mm. pressure; it is alkaline to litmus, and absorbs carbonic anhydride; the yellow *aurochloride* melts at 109° ; the *methiodide*, melting at 260° , is identical with the substance obtained by the direct action of methylic iodide on decahydroquinoline. Treated with aqueous potash and methylic chlorocarbonate, decahydroquinoline yields *methylic decahydroquinolinecarbamate*, $C_9H_{16}N \cdot COOMe$; this is a colourless oil, boiling at $277-277.5^\circ$ under 712 mm. pressure, and having an odour resembling that of peppermint. When added, in acetic acid solution, to a cooled acetic acid solution of fuming nitric acid, it yields a yellowish *mononitro-derivative* melting at 109° , and forming, with bromine, a *bromo-derivative* that melts at 170° . When it is treated with a larger quantity of undiluted fuming nitric acid at 10° , it is oxidised to *carbozylmethylhexahydroorthoamidophenylacetic acid*,



melting at 153.5° . When this is hydrolysed with hydrochloric acid, it yields a hydrochloride from which, by treatment with silver oxide, there is obtained a substance of high melting point that is possibly hexamethyleneoxindole, $C_6H_{10} \begin{smallmatrix} CH_2 \\ NH \end{smallmatrix} > CO$.

Benzoyldecahydroquinoline, prepared by treating the base with potash and benzoic chloride, melts at 96° , and boils at $352-354^\circ$ under 714 mm. pressure. When oxidised with alkaline permanganate, it yields *maleinoid benzoylorthoamidohexahydrohydrocinnamic acid*, $NHBz \cdot C_6H_{10} \cdot CH_2 \cdot CH_2 \cdot COOH$, melting at 196° , together with small quantities of benzamide and benzoic acid, and an acid (? benzoyl-orthamidohexahydrocinnamic acid) melting at 153.5° , obtained in one experiment only, from which, after hydrolysis with hydrochloric acid, a substance was obtained that melts at 127° , and forms a hydrochloride. When the above-mentioned maleinoid benzoyl-acid is hydrolysed with hydrochloric acid at 160° , it yields *hexahydrohydrocarbostyryl*, $C_6H_{10} \begin{smallmatrix} CH_2 \cdot CH_2 \\ NH \cdot CO \end{smallmatrix}$; this forms monoclinic crystals ($\alpha : b : c = 1.3178 : 1 : 0.9953$; $\beta = 73^\circ 34'$), melts at 151° , and sublimes above 100° ; its physiological action resembles that of oxypiperidine. Its *benzoyl derivative*, melting at 85° , is obtained by

warming the maleinoid benzoyl-acid for four hours with acetic chloride on the water bath; when hydrolysed with soda, it yields the maleinoid benzoyl-acid; with hydrochloric acid, first this acid, and finally benzoic acid and hexahydrohydrocarbostyryl. This last substance, when dissolved in aqueous soda and treated with benzoic chloride at 0° , yields *fumaroid benzoylorthoamido-hexahydrohydrocin-namic acid*, which melts at 205° , but with all reagents yields the same products as the maleinoid isomeride described above; the isomerism is of the same kind as that of the hexahydrophthalic acids.

It will be seen that, generally speaking, decahydroquinoline and hexahydrohydrocarbostyryl are respectively analogous, in their properties and reactions, to piperidine and oxypiperidine, to which they stand in the same relation as quinoline to pyridine. C. F. B.

Phenylisoxazolonimide. By E. v. MEYER (*J. pr. Chem.*, [2], 49, 504).—v. Rothenburg (this vol., i, 384) has overlooked the paper of Burns (Abstr., 1893, i, 314) which contains an account of the reaction between hydroxylamine and cyanacetophenone.

A. G. B.

n-Phenylpyrazolene. By R. v. ROTHENBURG (*Ber.*, 27, 1265—1266).—The author points out that one of the alternative constitutions assigned to the phenylpyrazolone (m. p. 118°) by Ruhemann and Morrell (this vol., i, 384) is identical with that which he assigned to the substance.

E. C. R.

Derivatives of Opiazone. By V. JACOBSON (*Ber.*, 27, 1418—1426).—When opiazone is heated with an alkali and methylic iodide (Abstr., 1893, i, 371), and the product evaporated with hydrochloric acid *n-methylnormethylopiazone*, $C_6H_7N_2O_3Me$, is obtained. This substance may also be prepared by heating opiazone with methylic iodide and methylic alcohol at 120° , and when pure melts at 144° (previously stated as 138°). The methylic group of one of the methoxyl-groups of the opiazone has, therefore, in this reaction wandered to the imido-group. A similar change occurs when opiazone is treated with benzylic chloride, *n-benzylnormethylopiazone*, $C_6H_7N_2O_3C_6H_5$, being formed. This substance melts at 199 — 200° , and, like the methylic derivative, gives a blue coloration with ferric chloride. When amylic bromide is employed instead of the benzylic chloride, *normethylopiazone*, $C_6H_5N_2O_3$, is the sole product. This substance can be obtained from opiazone by the action of acids and by various other reactions. It crystallises in long, colourless needles, melts at 226° , and readily dissolves in water. It forms a yellow solution in alkalis, and gives a blue coloration with ferric chloride.

Acetylnormethylopiazone, $C_6H_7N_2O_3Ac$, is formed, along with the *diacetyl* compound, by the action of acetic anhydride on normethylopiazone. When the crude product is heated to about 200° , the *diacetyl* compound is decomposed with formation of acetic anhydride, and the pure monacetyl compound can then be obtained by recrystallisation. It forms prisms which melt at 209 — 210° , and gives no reaction with ferric chloride.

Noropiazone, $C_8H_8N_2O_3$, is obtained by heating opiazone with hydriodic acid; it forms small, colourless needles, melts at $302-305^\circ$, and is very sparingly soluble in water. *Triacetylnoropiazone*, $C_8H_8N_2O_3Ac_3$, melts at $184-186^\circ$, and when heated with water is partially decomposed. *n-Methylnoropiazone*, $C_8H_8N_2O_3Me$, is formed by molecular change when normethylopiazone is heated with hydriodic acid at 150° . It has a yellowish colour, and melts at 310° ; with ferric chloride it gives a blue coloration.

Nitro-opiazone, $\begin{array}{c} OMe \cdot C \cdot C(OMe) \cdot C \cdot CO \cdot NH \\ | \qquad \qquad \qquad | \\ CH \cdot C(NO_2) \cdot C \cdot CH \cdot N \end{array}$, is prepared by the direct nitration of opiazone. It crystallises in matted, yellow needles, melting and decomposing at 248° . The same compound may be obtained by the action of hydrazine on nitro-opiamic acid. Nitro-opiazone possesses acid properties, and forms a red, soluble *potassium* salt, $C_{10}H_8N_2O_5K$, the imido-hydrogen being replaced. *n-Methylnitronormmethylopiazone*, $NO_2 \cdot C_8H_8N_2O_3Me$, is formed when nitro-opiazone is heated with methylic iodide and methylic alcohol at 150° . It crystallises in red needles, decomposes at 286° , and gives a greenish-brown coloration with ferric chloride. Like nitro-opiazone, it is an acid, and forms a *potassium* salt.

This red *n*-methylnitronormmethylopiazone is accompanied by a yellow isomeric compound, which crystallises in prisms and melts at 186° . The isomerism is probably due to the participation of both of the methoxyl groups in the molecular change.

Chloropiazone cannot be converted into chloronormmethylopiazone, since the chlorine atom enters into the reaction, and normethylopiazone is formed. A. H.

Morphine. By L. KNOER (*Ber.*, 27, 1144—1150; compare *Abstr.*, 1889, 417, 905).—It has been previously shown that methylmorphimethine, on treatment with acetic anhydride, is resolved into methoxyhydroxyphenanthrene and hydroxyethyldiethylamine, the amorphous base, which is also formed, proves to be optically isomeric with methylmorphimethine, and is termed the β -form. It differs from α -methylmorphimethine (m. p. 118.5°) as follows: It is more readily soluble in ether, the specific refractive power $[a/D]^{17} = +437.3$ ($c = 3.746$), with sulphuric acid it gives a violet coloration, changing successively to blue and green on dilution; the lethal dose is twice as great. The *hydrochloride* and *tartrate* are readily soluble; the *methiodide* crystallises in needles, melts at 297° , and was previously obtained by Hesse, who, however, overlooked its optical relationship to the α -derivative; the specific rotatory power $[\alpha/D]^{17} = +227.45$ ($c = 1.248$). The acetyl derivative and its *methiodide* are not crystalline. Methylmorphimethine is completely decomposed by hydrochloric acid, but, by the action of hydrogen chloride at 180° , it is resolved into dihydroxyphenanthrene, methylic chloride, water, and probably chlorethyldiethylamine; part of the base is recovered as β -methylmorphimethine. The dihydroxyphenanthrene was identified by its acetyl-derivative (m. p. 158°), and has been previously prepared by v. Gerichten and O. Fischer. On distillation with zinc dust, methylmorphimethine yields 10 per cent. of its weight of phen-

anthrene, whilst from morphine only 3—4 per cent. is formed. These results are in complete accord with the formula



for methylmorphimethine previously suggested by the author.

Methylmorphimethine is readily prepared by the following method: Sodium (24 grams) is dissolved in methylic alcohol (1 litre), commercial morphine (303 grams), and methylic iodide (350 grams) added, the yield of codeine methiodide is 90 per cent. of the theoretical. The iodide (400 grams) is dissolved in water (2 litres) and boiled for 10 minutes with 25 per cent. soda (500 c.c.). The yield of pure base is 80 per cent. of the theoretical. Codeine methiodide decomposes at 270° ; its specific refractive power $[\alpha_D]^{17} = -81.9^\circ$. α - and β -methylmorphimethine differ considerably from morphine and codeine in their physiological action; they lower the blood pressure, reduce the heart's activity, and possess no anæsthetic or soporific action, neither do they cause contraction of the pupil.

J. B. T.

Codeine. By W. GÖBLICH (*Arch. Pharm.*, 232, 154—160; compare Abstr., 1893, i, 675).—Dicodeine ethylene bromide,



has been obtained in crystals which soften at 155 — 157° , and melt at 177 — 179° . It remains colourless with cold sulphuric acid, becoming blue when heated; a yellow coloration is produced by nitric acid. Erdmann's reagent gives a yellow colour, changing to blue on heating; with vanadic anhydride and sulphuric acid a yellow coloration is developed which turns green, and finally blue on heating; the same effect is produced by Fröhde's reagent. Dicodeine ethylene bromide gives Faby's reaction for codeine, and when warmed with concentrated sulphuric acid and a small quantity of cane sugar, produces a brilliant purple coloration. Its aqueous solution is lævorotatory, and gives $[\alpha]_D = -97.06^\circ$ at 20° . Dicodeine ethylene bromide belongs to the rhombic system, $a : b : c = 0.9601 : 1 : 0.8292$.

Dicodeine ethylene chloride, $(\text{C}_{18}\text{H}_{21}\text{NO}_2)_2 \cdot \text{C}_2\text{H}_4\text{Cl}_2 + 4\text{H}_2\text{O}$, is obtained by treating the above-mentioned substance with silver chloride. It forms colourless needles which soften at 164 — 168° , and melt at 182 — 192° ; the colour reactions correspond exactly with those of the previous compound.

M. O. F.

Constitution of Cinchonine. By W. v. MILLER and G. RÖHDE (*Ber.*, 27, 1187—1190).—When methylcinchonine and phenylhydrazine are heated together in acetic solution a crystalline *hydrazone*, $\text{C}_{28}\text{H}_{32}\text{N}_4$, is formed which melts at 151.5° . It is basic in properties, and dissolves in acids. Ethylcinchonine, methylquinine, and methylquinidine behave similarly. The *hydrazone*, $\text{C}_{27}\text{H}_{30}\text{N}_4$, from ethylcinchonine melts at 152 — 153° . The *hydrazones* from methylquinidine and methylquinine both melt at 135 — 136° , have the same crystalline form, and appear to be identical. These results show that in methylcinchonine the oxygen is in the aldehydic or ketonic form.

The authors then discuss the bearing of these facts and the results recently obtained by Skraup, Koenigs, and others on the question of the constitution of one part of the cinchonine molecule. L. T. T.

Constitution of Cinchonine. By W. v. MILLER and G. ROHOR (*Ber.*, 27, 1279—1281; compare preceding Abstr.).—Cinchonine, when heated with dilute acetic acid for 24 hours at 105°, yields an oil having the appearance of methylquinine and methylquinidine. It gives a purple coloration with diazobenzene sulphonic acid and a few drops of alkali; when warmed with moist silver oxide in alcoholic solution, it reduces it with the formation of a mirror, and yields a hydrazone with phenylhydrazine. When treated with methylic iodide and soda, it yields methylcinchonine (m. p. 74—75°) and its methiodide. The above reactions are in accordance with the authors' views on the constitution of cinchonine. E. C. R.

Non-existence of Chenopodine. By G. BAUMERT and K. HALPERN (*Arch. Pharm.*, 231, 648—653).—See this vol., ii, 370.

Cholic acid. By K. LANDSTEINER (*Zeit. physiol. Chem.*, 19, 285—288).—Bromine acts destructively on dry cholic acid; it is slowly absorbed by a solution in acetic acid with evolution of hydrogen bromide.

Bromdehydrocholic acid, $C_{24}H_{42}BrO_6$, is obtained by the bromination of dehydrocholic acid in acetic acid solution; it crystallises in needles, and melts and decomposes at 171—173°. Small, octahedral crystals melting at 160—163° were also obtained, and seemed to be a mixture of the foregoing substance with an isomeride or other substance. The bromination can be carried further, but the crystalline product obtained does not seem to have been examined.

Bilanic acid also seems to yield a substitution derivative with bromine.

When treated with fuming nitric acid at 0°, cholic acid is converted into dehydrocholic acid. A. J. G.

Action of Zinc and its Salts on Blood and Blood-pigment. By E. GRAHE (*Chem. Centr.*, 1894, i, 636—637; from *Arch. Pharmak. Inst. Dorpat*, 9, 155—174).—By shaking blood with zinc dust Kobert has prepared zinc-parahæmoglobin. This substance resembles oxy-hæmoglobin in spectrum and in solubility in dilute ammonia; it resembles methæmoglobin in colour and other properties. It differs from both in certain solubilities and colour reactions. It can be prepared by the use of many zinc salts, both from blood and solutions of crystalline blood-pigment. It is precipitated by hydrochloric acid from alkaline solutions, and the formula $C_{726}H_{1138}Zn_2S_2FeO_{210}$ is given to it. It is not toxic, and like hæmoglobin is absorbed, and of use in the treatment of chlorosis. W. D. H.

Organic Chemistry.

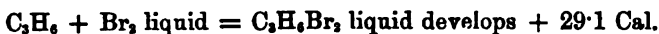
Possible Number of Isomerides of a Carbon Compound. By DELANNOY (*Bull. Soc. Chim.*, [3], 11, 239—248).—The author has investigated the general problem respecting the possible number of isomerides of a carbon compound by a process somewhat similar to that used by Cayley; his results, however, differ slightly from those of the latter. W. J. P.

Aspen Tar. By W. ADOLPHI (*Arch. Pharm.*, 232, 321—328).—Aspen tar from *Populus tremula* is a commercial article in Central Russia. It is a black, oily liquid of sp. gr. 1·0586 at 15°, and has a peculiar and unpleasant odour; the crystalline leaflets which are visible in the body of the liquid do not give the reactions of pimaric acid. The tar is completely soluble in absolute alcohol, acetone, or alkalis, and 72 per cent. of it distils below 300°, leaving a little pitchy residue. The distillate contains acetic, propionic, butyric, valeric, and caproic acids. The phenols present form 16·7 per cent. of the tar distilled, and boil at 200—290°, more than half distilling at 250—270°; the fraction boiling at 230° gives the catechol reaction, whilst the portions boiling at higher temperatures give the pyrogallol reaction with ferric chloride; guaiacol is also present. The hydrocarbons boil at 100—340°, the major part distilling at 210—260°; paraffin melting at 38° was isolated from the fraction boiling at 290—340°.

W. J. P.

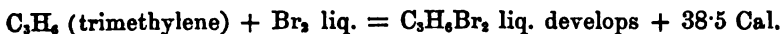
Trimethylene and Propylene, and a New Class of Hydrocarbons: Dynamic Isomerism. By BERTHELOT (*Compt. rend.*, 118, 1115—1123).—The author has previously shown that the heat of formation of propylene from its elements is -9·4 Cal., and of trimethylene -17·1 Cal. From Longuinine's determinations of the heats of combustion, it follows that the heats of formation of the two alcohols from their elements are +80·6 Cal. and +78·6 Cal. respectively.

Direct determination of the heat developed by the combination of bromine with propylene shows that



This value is almost identical with the corresponding value in the case of ethylene +29·3 Cals., and it follows that propylene is the true homologue of ethylene. There is, moreover, the normal difference between the heats of formation of the two hydrocarbons.

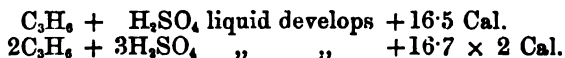
In the case of trimethylene, the number obtained is much higher.



Both dibromides develop a further quantity of heat in contact with an excess of bromine, owing to the formation of perbromides, and the

values obtained are somewhat higher in the case of trimethylene, but the difference is not great.

In the calorimeter, the absorption of propylene by sulphuric acid takes place less readily than in an *eprouvette*, and it is not possible to obtain complete saturation of the acid. The results with very different proportions of acid do not, however, differ materially.



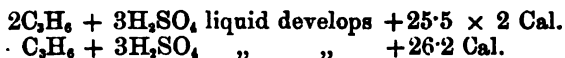
Some years ago, with a large excess of sulphuric acid, the author obtained the value +19.0 Cal. If the results are calculated for a dilute acid (which does not actually absorb the gas), it is found that



a number practically identical with that obtained with ethylene, +16.9 Cal.

When sulphuric acid completely saturated with propylene is brought in contact with water, there is practically no development of heat (this vol., i, 393), but if a considerable quantity of free sulphuric acid is present, precautions must be taken to avoid any appreciable rise of temperature, or the propylene sulphate is decomposed and isomerides of propylene are formed. Trimethylene sulphate, although more stable in presence of water, likewise decomposes if any rise of temperature is allowed to take place when the partially saturated sulphuric acid is mixed with water.

In the case of trimethylene sulphate, the values obtained are



Hence, for the same proportions of gas absorbed, the values are for propylene +16.7 Cal., and trimethylene +25.5 Cal.

It will be observed that the heats of formation of the trimethylene compounds are from 8 to 10 Cals. in excess of the heats of formation of the corresponding propylene compounds, whereas in the case of the hydrocarbons themselves the difference has a similar numerical value but is opposite in sign. The heats of formation of the two series of compounds from their elements are, however, practically the same for the corresponding members. Similar differences have been observed by the author and Matignon between terebenthene and its isomerides. The former has the lower heat of formation from its elements, but the heat of formation of its hydrochloride by the action of hydrogen chloride is double that of its isomerides, whilst the heats of formation of the hydrochlorides from their elements are almost identical.

Trimethylene and terebenthene, respectively, differ from their isomerides in a manner that cannot be represented by plane formulæ. They represent new types, characterised by their mobility and their reserves of energy. The author terms them *dynamic isomerides*. The explosive liquid polymerides of acetylene perhaps belong to the same class.

C. H. B.

Rectification of Alcohol. By E. SOREL (*Compt. rend.*, 118, 1213—1215).—The author has previously shown that in the rectification of alcohol the volatile impurities ascend to higher levels, or descend towards the still, according as the difference $K - P/p$ is positive or negative, K being the ratio of the weight of the impurity in 1 kilo. of the vapour and in 1 kilo. of the liquid in contact at the particular level, P the weight of the liquid that flows back, and p the weight of the vapour that passes upwards at that level. He has now determined the values of K for fermentation isoamylic alcohol, ethylic formate, methylic acetate, ethylic acetate, ethylic isobutyrate, ethylic isovalerate, isoamylic acetate, and isoamylic isovalerate, and the results are given in a table. The value of K increases with increase of molecular weight and rise of boiling point, but there is no definite relation between the three. In each group, however, the value of K increases the more dilute the alcohol. Ethylic formate and methylic acetate are soluble in water or dilute alcohol, and in these cases the ratio of the values of K for a given alcoholic strength increases continuously with the proportion of water. Ethylic isovalerate and isoamylic acetate are insoluble in dilute alcohol, and the ratio passes through a maximum. Ethylic isobutyrate and the ethereal salts of higher molecular weight can only be retained in the rectifying column in presence of strong alcohol. C. H. B.

Constitution of Licareol. By P. BARBIER and L. BOUVEAULT (*Compt. rend.*, 118, 1208—1211).—When licareol is gradually mixed with sufficient chromic acid mixture to yield 2 atoms of oxygen for each molecule of the alcohol, it yields acetone, licaraldehyde or licarhodol, a methyl heptylene ketone, acetic and formic acids, and methylheptyleneketonecarboxylic acid. With an excess of boiling chromic acid mixture, the products are formic and acetic acids and terebic acid.

The licaraldehyde boils at 111—112° under a pressure of about 13 mm., and yields an oxime boiling at about 145° under a pressure of 12 mm., which in its turn yields licarionitrile, boiling at 110—111° under a pressure of 13 mm. It yields with paramidophenol a crystalline compound, $C_{10}H_{18}N \cdot C_8H_7 \cdot OH$. When boiled with glacial acetic acid, it yields paracymene.

The methyl heptylene ketone is identical in all its properties with the natural product.

The formation of terebic acid indicates that the constitution of licareol is more probably $CMe_3 \cdot CH \cdot CH_2 \cdot CH(CH_2 \cdot OH) \cdot CMe \cdot CH_3$, than that previously ascribed to it. Licareol and lemonol (geraniol) yield practically the same products on oxidation, and the only reasons for supposing that they have different constitutions are that the former is optically active whilst the latter is inactive, and the two aldehydes yield, with paramidophenol, compounds which have different melting points. It is possible, although not probable, that lemonol is a racemic compound. C. H. B.

Geraniol from Oil of "Andropogon Schoenanthus." By P. BARBIER and L. BOUVEAULT (*Compt. rend.*, 118, 1154—1157).—When

geraniol from oil of *Andropogon Schœnanthus* is allowed to fall drop by drop into a boiling chromic acid mixture capable of yielding 10 atoms of oxygen for each molecule of alcohol, the products are carbonic anhydride, acetone, acetic and formic acids, and terebic acid (m. p. 174°). No valeric acid is formed.

When a quantity of chromic acid mixture, capable of yielding 2 atoms of oxygen for each molecule of the alcohol, is added little by little to the geraniol, the products are geranaldehyde, boiling at 113° under a pressure of 13 mm., and identical with so-called citriodorice aldehyde; methyl heptylene ketone, boiling at 169—172°, possessing all the properties of the natural product, and not yielding the crystalline bromine derivative described by Tiemann and Semmler; paracymene, formed as a secondary product by the action of the sulphuric acid on the geranaldehyde; and methylheptyleneketone-carboxylic acid.

With potassium permanganate, the geraniol yields no valeric acid. It follows that the geraniol of *Andropogon Schœnanthus* has the constitution $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$.

Oil of pelargonium is quite different from oil of *A. Schœnanthus*, and hence it is undesirable to retain the name of geraniol for the oil contained in the latter. The author proposes to call it *lemonol*.

C. H. B.

Inverting Action of Glycerol. By E. DONATH (*J. pr. Chem.*, [2], 49, 546—548).—Consideration of Zulkowski's work on the transformation of starch in hot glycerol (Abstr., 1889, 116) led the author to ascertain whether glycerol has any hydrolytic action on sugars. It was found that cane sugar, milk sugar, maltose, and raffinose are hydrolysed when heated at 120—130° with aqueous glycerol in the same manner as they are hydrolysed by dilute acids; furthermore, the order of facility with which the hydrolysis occurs is the same, whether glycerol or acid be the hydrolytic agent. Anhydrous glycerol has comparatively little hydrolytic action, whilst glycerol containing 20 per cent. of water has a considerable action; from this the author concludes that the hydrates of glycerol contained in the aqueous solution are dissociated at the temperature employed, and that it is the nascent molecules of water of hydration which effect the hydrolysis. It is hoped that a general theory of hydrolytic action may be deduced from these observations.

A. G. B.

Ethylnitrolic acid and Nitromethane. By V. METER (*Ber.*, 27, 1600—1602).—*Benzoyl ethyl nitrolic acid*, $\text{NO}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{OBz}$, may be readily prepared by agitating ethyl nitrolic acid with caustic soda and benzoic chloride. It crystallises from toluene in small, white plates, and melts at 137° without decomposing. When boiled with dilute sulphuric acid, it decomposes into nitrous oxide, and acetic and benzoic acids. The compound may be preserved without undergoing any change, whilst the nitrolic acids themselves soon decompose.

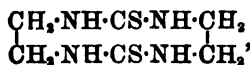
Sodionitromethane has hitherto never been obtained pure, the composition of the salt prepared by means of alcoholic soda always

agreeing with the formula $\text{CH}_3\text{Na}\cdot\text{NO}_2 + 2\frac{1}{2}\text{H}_2\text{O}$. When, however, a solution of sodium ethoxide is added to a solution of nitromethane in ether, the pure substance is at once precipitated. The compound thus prepared is much more violently explosive than that previously obtained.

A. H.

Action of Thiocarbonic Chloride on Ethylenediamine. By M. JAFFÉ and B. KÜHN (*Ber.*, 27, 1663—1666).—The action takes place according to the equation $2\text{CSCl}_2 + 2\text{C}_2\text{H}_4(\text{NH}_2)_2 = \text{C}_6\text{H}_{10}\text{N}_4\text{S} + 4\text{HCl} + \text{H}_2\text{S}$. The substance $\text{C}_6\text{H}_{10}\text{N}_4\text{S}$ appears to have the con-

stitution $\begin{array}{c} \text{CH}_3\cdot\text{N}:\text{C}\cdot\text{NH}\cdot\text{CH}_3 \\ | \qquad \qquad | \\ \text{CH}_3\cdot\text{NH}\cdot\text{C}:\text{N}\cdot\text{CH}_3 \end{array}$, and probably results from the elimination of H_2S from the tautomeric form of the compound



which may be supposed to be first formed. It readily loses its sulphur under the influence of mild oxidising agents, such as bromine water, yielding a substance, the hydrobromide of which, $\text{C}_6\text{H}_{10}\text{N}_4\cdot\text{HBr}$, was obtained crystallised. It forms various salts, of which the formulæ and melting points (with decomposition) are:— $\text{C}_6\text{H}_{10}\text{N}_4\text{S}\cdot\text{HCl}$; 270°. $\text{C}_6\text{H}_{10}\text{N}_4\text{S}\cdot\text{HNO}_3$; 246—247°. $\text{C}_6\text{H}_{10}\text{N}_4\text{S}\cdot\text{H}_2\text{SO}_4$; 230—231°. $\text{C}_6\text{H}_{10}\text{N}_4\text{S}\cdot\text{HgCl}_2$. $\text{C}_6\text{H}_{10}\text{N}_4\text{S}\cdot\text{HCl}\cdot 2\text{HgCl}_2$. $\text{C}_6\text{H}_{10}\text{N}_4\text{S}\cdot\text{C}_6\text{H}_5\text{N}_3\text{O}_7$ (picrate); 229—230°. C. F. B.

Choline and Muscarine. By G. NOTHNAGEL (*Arch. Pharm.*, 232, 261—306; compare *Abstr.*, 1892, 219, 806; 1893, i, 297).—*Acetyl ethyl trimethyl ammonium platinochloride*, $(\text{OAc}\cdot\text{C}_2\text{H}_5\cdot\text{NMe}_3)_2\text{PtCl}_6$, crystallises in small, yellow needles melting at 223—224°. Choline only reacts with acetic chloride at 100°, and the acetyl compound is readily hydrolysed.

On heating choline chloride with benzoic chloride at 100°, distilling off the excess of the latter, and treating the residue with platinic chloride in aqueous solution, yellow, crystalline threads of a *platinochloride*, $(\text{OBz}\cdot\text{C}_2\text{H}_5\cdot\text{NMe}_3)_2\text{PtCl}_6$, are deposited; it melts at 206°. The *aurochloride*, $\text{OBz}\cdot\text{C}_2\text{H}_5\cdot\text{NMe}_3\cdot\text{AuCl}_4$, crystallises in flat, yellow needles melting at 183°. No reaction between choline and glycollic, salicylic, or ethylenelactic acid could be brought about under various conditions.

On heating an aqueous solution of choline with hydroxyisobutyric acid, a substance is formed, which yields a *platinochloride* of the constitution $\text{NMe}_3\text{Cl}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{CMe}_2\cdot\text{COO}\cdot\text{C}_2\text{H}_4\cdot\text{NMe}_3\text{Cl}\cdot\text{PtCl}_4 + 2\text{H}_2\text{O}$; it crystallises in needles melting at 221°. No aurochloride could be prepared either directly or from the platinochloride, the latter, when treated with gold chloride, decomposing with formation of choline aurochloride. Similarly, on heating choline solution with hydroxyvaleric acid and treating the product with platinic chloride, a *platinochloride* of the composition $\text{NMe}_3\text{Cl}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_4\text{H}_7\cdot\text{COO}\cdot\text{C}_2\text{H}_4\cdot\text{NMe}_3\text{Cl}\cdot\text{PtCl}_4 + 2\text{H}_2\text{O}$,

is obtained; it crystallises in long, compact needles melting at 223—224°. No aurochloride could be prepared.

The rest of the paper consists principally of a repetition and confirmation of previous work on this subject. W. J. P.

Diazomethane. By H. v. PECHMANN (*Ber.*, 27, 1888—1891).—When nitrosomethylbenzamide, nitrosomethylurethane, and similar nitroso-derivatives of methylamine are treated with alkalis, a yellow gas is formed, along with other products. This gas is *diazomethane*, $\text{CH}_2 < \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix}$. It is odourless, but very poisonous, and has hitherto only

been examined in ethereal solution. The yellow, ethereal solution is at once decolorised by dilute acids or by water, the whole of the nitrogen being evolved. Iodine solution also decomposes it, nitrogen being evolved and methylene iodide formed. Like ethylic diazoacetate, it combines with ethylic fumarate, and forms *methylic pyrazoline-4:5-dicarboxylate*, which crystallises in lustrous, rhombic tablets melting at 97°. When this substance is heated with dilute hydrochloric acid, hydrazine hydrochloride is produced. When the pyrazoline-derivative is distilled, decomposition occurs, about 80 per cent. of the nitrogen being evolved, and *cistrans-trimethylene-1:2-dicarboxylic acid* passing over.

Diazomethane behaves towards silver nitrate and Fehling's solution in the same manner as ethylic diazoacetate, reduces mercuric oxide in the cold, and rapidly bleaches and destroys cork.

Diazoethane has been prepared in a similar manner, and has similar properties: when it is treated with mercuric oxide, the smell of mercuric ethide is perceptible.

A more detailed account will be shortly published.

A. H.

Compounds of Formaldehyde with Polyhydric Alcohols. By M. SCHULZ and B. TOLLENS (*Ber.*, 27, 1892—1894).—When the polyhydric alcohols are heated on the water-bath with a 40 per cent. solution of formaldehyde and concentrated hydrochloric acid, a reaction occurs, and methylene ethers or formacetals are produced.

Mannitoltriformacetal, $\text{C}_6\text{H}_8\text{O}_4(\text{CH}_2)_3$, forms needles melting at 227°, and sparingly soluble in water and alcohol. It is *lævo-rotatory*. *Sorbitoltriformacetal* melts at 206°, and otherwise resembles the mannitol compound. *Adonitoldiformacetal*, $\text{C}_6\text{H}_8\text{O}_4(\text{CH}_2)_3\text{OH}$, melts at 145°, may be sublimed in a vacuum, and is more readily soluble than the mannitol-derivative. One hydroxyl group is left in the compound, since it forms a *benzoate* which melts at 104°. *Penta-erythritoldiformacetal*, $\text{C}_6\text{H}_8\text{O}_4(\text{CH}_2)_3$, forms large crystals melting at 50°, very readily soluble in water. Erythritol yields a similar compound. *Glycerolformacetal*, $\text{C}_3\text{H}_8\text{O}_2(\text{CH}_2)_3\text{OH}$, is a liquid boiling at 191—193°, and forms a *benzoate* melting at 70°.

A. H.

Condensation of Methyl Ethyl Ketone with Malonic acid. By W. MASSOT (*Ber.*, 27, 1574—1577).—When methyl ethyl ketone and malonic acid are heated together with acetic anhydride, the pro-

duct consists of two portions, one crystalline, the other oily. The crystalline product is a monobasic acid of the formula $C_6H_{10}O_4$, which crystallises from light petroleum in small prisms melting at $76-77^\circ$. The barium salt $(C_6H_9O_4)_2Ba + H_2O$, forms microcrystalline crusts. When treated with alkaline hydroxylamine solution, the acid yields a monoxime, $C_6H_{10}O_3N \cdot OH$, which forms small, prismatic crystals, and melts at $195-196^\circ$. A dioxime could not be obtained, neither could any evidence of the presence of a hydroxyl-group be found; the constitution of the acid, therefore, remains unsettled, but it appears to be the homologue of the acid, $C_5H_8O_4$, obtained by the author from acetone and malonic acid (this vol., i, 356), and, like this, is only formed in very small quantity.

The oily product contains a certain amount of the above acid, together with β -ethylcrotonic acid, $OMeEt \cdot CH \cdot COOH$, which, however, could not be obtained pure. A. H.

Diamidopropionic acid. By E. KLEBS (*Zeit. physiol. Chem.*, 19, 301—338; compare *Abstr.*, 1893, i, 686).—The author gives a table showing the behaviour of diamidopropionic acid towards reagents. The mercuric salt, $(NH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COO)_2Hg \cdot 4H_2O$, is obtained in colourless cubic crystals; both this and the copper salt have an alkaline reaction, and give no precipitates with caustic soda even on boiling. The sulphate crystallises in needles containing $\frac{1}{2}H_2O$, and melts and decomposes at $226-228^\circ$. The nitrate crystallises without water, and melts and gives off gas at 170° . The acetate is obtained in small, anhydrous, orthorhombic plates melting at $110-112^\circ$; on prolonged heating at 100° , it melts and gives off acetic acid. The oxalate crystallises in small needles containing $2H_2O$, and melts and decomposes at $175-178^\circ$. The picrate decomposes at 200° , and resembles picric acid in appearance; it crystallises with $2H_2O$. The platinochloride crystallises in tiny cubes containing $1H_2O$.

Diamidopropionic acid yields glyceric and oxalic acids when treated with nitrous acid.

Dibenzoyldiamidopropionic acid, $NHBz \cdot CH_2 \cdot CH(NHBz) \cdot COOH$, is prepared by treating diamidopropionic acid hydrochloride with benzoic chloride and caustic soda; it crystallises in colourless needles melting at $195-197^\circ$, and is very sparingly soluble in water. The barium salt forms white, anhydrous crystalline crusts.

Attempts to synthesise diamidoacetic acid by the action of ammonia on dihalogenacetic acids or their ethylic salts, by the reduction of ethylic formazylcarboxylate and, indirectly, by the action of mercuracetamide on ethylic diiodoacetate were unsuccessful.

W. J. P.

Action of Water on Soap. By F. KRAFFT and A. STERN (*Ber.*, 27, 1747—1754).—In view of the recent theories as to the cleansing action of soap (see next abstract), the authors have repeated and extended Chevreul's experiments on the action of water on soap, and have confirmed the results arrived at by him. When neutral sodium palmitate, $NaC_{16}H_{31}O_2$, containing 8.27 per cent. of sodium, is boiled up with water and the liquid allowed to cool, the mass which separates contains less sodium as the amount of water employed is

increased. When about 900 parts of water are used, the mass which separates has the composition of sodium bipalmitate,

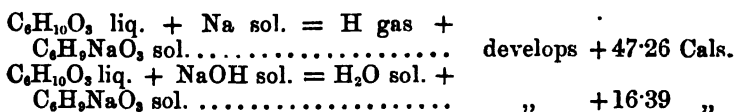


whilst, with smaller quantities of water, any desired mixture containing more sodium than this may be obtained. The filtrate from the solid mass has a strongly alkaline reaction, and is almost free from fatty acid, the addition of a mineral acid producing only a faint turbidity, so that basic salts are certainly not present. A hot dilute solution of sodium palmitate has a milky appearance, which is due to the presence of free palmitic acid in the form of oily drops suspended in the liquid. When such a solution is extracted with toluene, pure palmitic acid goes into solution. The hot solution therefore contains free fatty acid as well as free alkali, which may be titrated with normal acid, in addition to a certain amount of undecomposed sodium salt.

Sodium stearate and sodium elaidate behave in a precisely similar manner, but sodium oleate is not so readily decomposed by hot water, only a very slight turbidity being caused by the addition of 900 parts of hot water. Sodium bioleate, on the other hand, is at once decomposed by water with separation of free oleic acid. A. H.

The Cleansing Action of Soap. By F. KRAFFT and A. STERN (*Ber.*, 27, 1755—1761; compare the foregoing abstract).—The authors criticise the view put forward by Rotondi [*Atti R. Accad. sci. Torino*, 19, 146 (1883)] and others, that when soap is acted on by water it is decomposed into an acid soap, which is almost insoluble in hot water, and a basic soap which remains dissolved. It follows from the experiments described in the foregoing abstract that when a soap is dissolved in a large amount of hot water, the sodium salts of palmitic, stearic, and elaidic acids separate out, along with an amount of the free acid which varies with the amount of water used, whilst the liquid contains free alkali and the sodium salt of oleic acid. No evidence of the existence of basic salts of the soap acids has been brought forward by the supporters of the theory, and none could be experimentally obtained by the authors. A. H.

Chemical Function and Constitution of Ethylic Acetoacetate. By DE FORCRAND (*Compt. rend.*, 118, 1101—1104).—The author has previously shown that the heat of dissolution of ethylic aceto-sodacetate is +4.39 Cals. (this vol., i, 356), and he now finds that the heat of dissolution of ethylic acetoacetate is +1.25 Cals., and its heat of neutralisation by sodium hydroxide +7.32 Cals. It follows that



If the first of these values is taken as the measure of the acid function, it is clear that it is lower than that of a true acid, but higher

than that of a tertiary alcohol. For the latter reason, the constitution of the compound cannot be $\text{CH}_3\cdot\text{C}(\text{ONa})\cdot\text{CH}\cdot\text{COOEt}$. The value of the acid function when calculated for the solid state of the original substance is not below 39 Cals. The only formula admissible would therefore seem to be $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOEt}$ and $\text{CH}_3\cdot\text{CO}\cdot\text{CHNa}\cdot\text{COOEt}$, although, in its chemical behaviour, the compound differs in many respects from ketones.

Attempts to prepare a pure sodium derivative of acetone, and thus determine directly the value of the ketonic function, were unsuccessful. All that is definitely known in this connection is (1) that the thermal value of the ketonic function is lower than that of the primary alcoholic function, and (2) the heat of neutralisation of a ketone is *nil*. It would seem certain that ethylic acetoacetate has not a ketonic function. There is, however, close agreement between the value of the phenolic function (+39.1 Cals.) and the heat of neutralisation of ordinary phenol (+7.96 Cals.) and the corresponding values for ethylic acetoacetate (+39 to 40 Cals. and +7.32 Cals. respectively). If it is assumed that the cause of the special acidity of the phenols is due not so much to the closing of the hydrocarbon chain as to the peculiar nature of the linkage of the carbon which is united with the hydroxyl group, it would seem that ethylic acetoacetate may be regarded as an open chain phenol with a degree of acidity intermediate between the true acids and alcohols. Its constitution would then be $\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{COOEt}$. C. H. B.

$\alpha_1\alpha_2$ -Dimethyladipic acids. By J. KITZING (*Ber.*, 27, 1578—1580).—When ethylene dibromide is heated with ethylic sodiomethylmalonate in the presence of toluene for 50—60 hours, *ethylic $\alpha_1\alpha_2$ -dimethyldicarboxyadipate*, $\text{C}_8\text{H}_{14}[\text{CMe}(\text{COOEt})]_2$, is obtained. It separates from light petroleum in well-developed crystals melting at 53—53.5°, and can be distilled under diminished pressure. *$\alpha_1\alpha_2$ -Dimethyldicarboxyadipic acid*, when rapidly heated, melts and decomposes at about 200°, but, when slowly heated, decomposes at about 170°, dimethyladipic acid (Zelinsky, *Abstr.*, 1892, 430) being formed; both the modification melting at 140—141° and that melting at 74—76° are obtained by recrystallising the product from water. A. H.

Bromomesaconic acid. By W. LOSSEN and O. GERLACH (*Ber.*, 27, 1851—1856).—As shown by Kekulé and others, citradibromoglutaric acid is resolved by the action of bases into bromomethacrylic acid, carbonic anhydride, and hydrogen bromide; under other conditions, propaldehyde, carbonic anhydride, and hydrogen bromide are formed. In continuation of their investigation of the influence exercised by the quantity and nature of the base on the decomposition of haloid acids (*Abstr.*, 1893, i, 142), the authors have found that by the action of concentrated (25 per cent.) soda (4 mol.) on citradibromoglutaric acid, *bromomesaconic acid*, $\text{C}_4\text{H}_5\text{Br}(\text{COOH})_2$, is formed, and crystallises from ether, on the addition of chloroform, in colourless stellate prisms melting at 220°. The yield is about 47 per cent. of the bromoglutaric acid employed. By the further action of soda bromomesaconic acid is converted into acetic acid; on reduction,

it yields glutaric acid, and, by heating above its melting point, bromocitraconic anhydride is produced. The *hydrogen potassium salt*, $C_6H_4BrO_4K$, crystallises in prisms; the *barium salt*, with $2H_2O$, is deposited in stellate needles or prisms; the *calcium salt*, $C_6H_4BrO_4Ca + H_2O$, does not crystallise very readily; the *zinc salt* is very characteristic, and may be used to purify the acid; it crystallises from water with $8H_2O$ in colourless prisms; the *silver salt* is deposited in slender needles. All these salts differ from the corresponding bromocitraconates.

J. B. T.

Solubility of Potassium Hydrogen Tartrate in Alcohol of various strengths. By J. A. ROELOFSEN (*Amer. Chem. J.*, 16, 464—467).—The following table gives the results obtained.

Milligrams of Potassium Hydrogen Tartrate dissolved in 10 c.c.

Temp.	Alcohol, percentage of.									Water.
	90.	80.	70.	60.	50.	40.	30.	20.	10.	
0°	6·2	6·4	4·9	6·0	6·0	6·2	7·0	10·8	17·3	30·1
5	5·5	6·0	5·1	6·0	6·8	6·8	7·1	13·2	18·8	32·0
10	6·2	6·2	5·1	5·8	6·4	7·0	8·6	16·0	27·0	41·1
15	5·3	6·2	6·2	6·2	5·5	7·7	8·8	15·8	23·9	44·3
20	6·4	6·4	6·2	6·4	7·0	9·6	11·8	17·1	29·3	49·0
25	4·7	5·5	6·0	6·8	7·0	10·3	11·7	21·4	36·4	54·1
30	4·7	6·0	6·8	7·5	8·5	11·0	13·1	24·8	39·9	69·2
35	1·9	5·1	5·9	6·8	9·0	12·4	18·8	28·7	49·3	83·8
40	1·7	5·3	5·8	7·0	10·2	14·9	23·1	37·7	53·6	95·9
45	1·7	5·3	6·0	7·9	10·7	16·5	25·8	44·2	72·6	112·8
50	1·5	5·1	6·0	8·1	12·8	19·0	29·7	53·6	87·2	124·8

L. T. T.

Dehydromucic acid from δ -Methylpyromucic acid. By H. B. HILL and H. E. SAWYER (*Ber.*, 27, 1569—1570).—When *w*-methylpyromucic chloride is treated with bromine in sunlight, *w*-dibromomethylpyromucic bromide, $C_6H_4Br_2O_3$, is formed; this crystallises in small, flat prisms, melts at 102° , and is readily soluble in benzene, less readily in cold light petroleum. Hot water converts it into δ -aldehydopyromucic acid, $C_6H_4O_4$, which crystallises with $1H_2O$ in long needles. The anhydrous acid forms colourless plates, is readily soluble in alcohol and water, and melts and decomposes at 205° , but may be partially sublimed when carefully heated. It is oxidised by silver oxide to dehydromucic acid, $C_6H_4O_6$, and the same change occurs when its alkaline solution is exposed to the air. *w*-Dibromomethylpyromucic acid, $C_6H_4Br_2O_3$, crystallises in thin tablets melting at 153° . It is difficult to obtain in quantity, and cannot therefore be used for the preparation of the aldehydo-acid.

A. H.

Succinimide. By E. H. MILLER (*J. Amer. Chem. Soc.*, 16, 433—462).—The author has obtained succinimide by heating together

ethylene cyanide and acetic acid at 180—200°; by heating together succinic acid and acetonitrile at 180—200°; and by heating together succinic acid and ethylene cyanide in molecular proportion. Determinations of the molecular weight were made by Raoult's method with water, ethylene bromide, and acetic acid as solvents, the average of all the determinations being 99·6, showing the correctness of the generally received formula. The solution gave a very light pink colour with methyl-orange, showing that it is neither strongly acid nor strongly alkaline.

As β -cyanopropionic acid, on heating, should give the unsymmetrical succinimide, the author endeavoured to obtain it by the action of potassium cyanide on potassium β -iodopropionate, and on ethylic β -iodopropionate. Only small quantities of a crystalline and almost neutral compound, $C_6H_{12}N_2O_6$, were obtained. The author believes that β -cyanopropionic acid is an unstable liquid, 2 mols. of which unite with water to form the above compound. This compound crystallises in needles soluble in boiling methyl and ethyl alcohols.

Ethylic β -cyanopropionate, a colourless, odourless liquid boiling at 228° and insoluble in water, was obtained by L. Henry (*Bull. Acad. roy. Belg.*, 1889, 18, 168).
L. T. T.

Acetonitriles. By W. ESCHWEILER (*Annalen*, 279, 39—44; compare this vol., i, 267).—Aqueous methylamine reacts with methylene cyanhydrin forming the nitriles of sarcosine and of methyldiglycolamidic acid. The product, when boiled with barium hydroxide solution and the filtrate evaporated with copper oxide, yields the copper derivatives of sarcosine (Strecker, *Annalen*, 157, 1) and of methyldiglycolamidic acid. The latter crystallises in small, anhydrous, bright blue, four-sided tables.

Methyldiglycolamidic acid, $NMe(CH_2\cdot COOH)_2$, forms colourless prisms and melts at 226—227° with decomposition. In the reaction between methylamine and methylene cyanhydrin, when a large excess of the former reagent is used, sarcosine nitrile, which cannot be distilled even under diminished pressure without decomposition, is the sole product; whilst, when an excess of methylenecyanhydrin is employed, methyldiglycolamidonitrile only is obtained. The latter boils at 70° under a pressure of 40 mm. If the hydrolysis of the last-named nitrile with barium hydroxide is incomplete, *methyldiglycolamidic acid amide*, $COOH\cdot CH_2\cdot NMe\cdot CH_2\cdot CONH_2$, is obtained; it crystallises from aqueous alcohol in long needles, and melts at 168°; the copper salt crystallises in deep blue, monhydrated, rhombic prisms, and is sparingly soluble in water.

Dimethylamine reacts very readily with methylene dicyanhydrin, the resulting nitrile being an almost odourless liquid, which boils at 137—138°, has a sp. gr. of 0·865 at 20°. When hydrolysed with barium hydroxide, the nitrile yields *dimethylglycocine*, the copper derivative of which, $(NMe_2\cdot CH_2\cdot COO)_2Cu + 3H_2O$, forms dark blue, rhombic crystals.

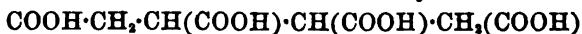
Trimethylamine does not react with methylene cyanhydrin.

A. R. L.

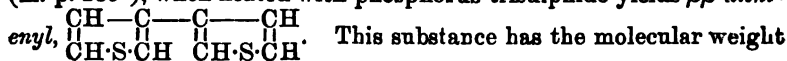
Trimethyltrimethylenetrisulphone. By E. LOMNITZ (*Ber.*, 27, 1667—1679).—Trimethyltrimethylenetrisulphone was prepared by oxidising α -trithioacetaldehyde with permanganate in the presence of sulphuric acid, and from it the potassium, sodium, barium, strontium, and silver salts were prepared. The same was done, starting with β -trithioacetaldehyde. The products were found to be identical in each case. It was hence inferred that only one modification of trimethyltrimethylenetrisulphone exists, and, in preparing other derivatives, the trisulphone from either source was indiscriminately used. The trisulphone still contains 3 atoms of displaceable hydrogen; only one of these, it is true, is capable of being displaced by a metal (forming salts that are readily decomposed by carbonic anhydride), but all three can be displaced by alkyl radicles. This is done by adding the iodide or chloride of the radicle to a solution of the trisulphone in caustic soda. In the aliphatic series, the more complex the radicle the less easily can it be introduced; a trimethyl-derivative is formed with ease, but only a little of a triethyl-, with much of a diethyl-derivative can be obtained, and only a little of a triallyl-derivative, whilst the isobutyl-group cannot be introduced at all. With aromatic radicles, the opposite appears to hold. All 3 hydrogen atoms of the trisulphone can further be displaced by chlorine or bromine, by the direct action of these elements. The formulæ and melting points of the new substances obtained are as follows.

Trimethyltrimethylenetrisulphone, $C_3H_3Me_3S_3O_6$, $(CHMe)_3(SO_2)_3$, or $CHMe \cdot SO_2 \cdot CHMe$, turns brown at 340° , sublimes at a higher temperature. $C_3H_3Me_3S_3O_6 \cdot K$. $C_3H_3Me_3S_3O_6 \cdot Na + 2H_2O$. $(C_3H_3Me_3S_3O_6)_2Ba + 6H_2O$. $(C_3H_3Me_3S_3O_6)_2Sr + 1$ or $6H_2O$. $C_3H_3Me_3S_3O_6 \cdot Ag + H_2O$. $C_3Me_3S_3O_6$, identical with the product from trimethylenetrisulphone (*Abstr.*, 1890, 26). $C_3Me_3Et_3S_3O_6$, 269° ; $C_3HMe_3Et_3S_3O_6$, $239-240^\circ$, yields a bromo-derivative, $C_3Me_3Et_3BrS_3O_6$, melting at 221° . $C_3Me_3Al_3S_3O_6$, 267° . $C_3Me_3(CH_2Ph)_3S_3O_6$, 268° , yields a trinitro-derivative, decomposing above 132° . $C_3Me_3(CH \cdot C_6H_4Me)_3S_3O_6$, 206° , yields a trinitro-derivative melting with decomposition at 191° . $C_3Me_3Br_3S_3O_6$, 240° ; $C_3Me_3Cl_3S_3O_6$, 270° . C. F. B.

Dithienyls. By K. AUWERS and T. V. BREDT (*Ber.*, 27, 1741—1747).—The sodium salt of butanetetracarboxylic acid,



(m. p. 189°), when heated with phosphorus trisulphide yields $\beta\beta$ -dithienyl,



of 166 in benzene solution, and crystallises in white, lustrous plates, which show a bluish fluorescence and melt at 132° . It is sparingly soluble in glacial acetic acid and light petroleum, more readily in other solvents. Its odour resembles that of naphthalene and also that of some sulphur compounds. It forms a yellow solution in concentrated sulphuric acid, and with sulphuric acid and isatin gives a greenish coloration, which becomes brownish-violet on heating. The butanetetracarboxylic acid melting at 236° also yields this substance,

the yield amounting to about 10 per cent. in both cases. Bromine added to a cold solution of the substance in glacial acetic acid probably forms a *dibromo-derivative*, but when the solution is heated a *tetrabromo- $\beta\beta$ -dithienyl*, $C_8H_2Br_4S_2$, is produced. This crystallises in lustrous white needles, melts at $137-138^\circ$, and does not give any coloration with sulphuric acid or isatin. *Hexabromo- $\beta\beta$ -dithienyl*, $C_8H_2Br_6S_2$, is formed by the continued action of bromine on a concentrated solution of dithienyl. It separates from benzene in short, compact prisms melting at 183° , and is insoluble in boiling alcohol.

$\beta\beta$ -Dithienyl is isomeric with the *ax-dithienyl* described by Töhl (this vol., i, 276). This substance forms a *dibromo-compound* which crystallises in large, thin, nacreous plates, melting at $142-143^\circ$, and a *tetrabromo-derivative* which crystallises in lustrous needles, and melts at $139-140^\circ$. A third dithienyl was obtained by Nahsen (Abstr., 1884, 1132; 1885, 50) by passing thiophen through a red hot tube. This substance, when submitted to fractional crystallisation and precipitation from glacial acetic acid, yields two compounds, one of which is probably identical with the *$\beta\beta$* , the other with *ax-dithienyl*.
A. H.

Constitution of Benzene. By A. CLAUS (*J. pr. Chem.*, [2], 49, 505—524).—A criticism of the recent paper by Brühl (this vol., i, 366) on this subject. The author cannot admit that the evidence adduced in that paper is favourable to Kekulé's formula and at variance with his own formula.
A. G. B.

Nitro-derivatives of Tertiary Butylbenzene. By A. BAUR (*Ber.*, 27, 1610—1611).—By the action of nitric acid (sp. gr. 1.48) on tertiary butylbenzene at low temperatures *nitrobutylbenzene*, $C_{10}H_{13}NO_2$, is formed, it is a viscid liquid, volatile with steam, and has a highly unpleasant smell. On warming with fuming nitric acid it is converted into the *dinitro-derivative*, $C_{10}H_{11}(NO_2)_2$, which is deposited from alcohol in yellow crystals melting at $61-62^\circ$. The *trinitro-derivative*, $C_{10}H_{11}(NO_2)_3$, is formed by the action of nitro-sulphuric acid on dinitrobutylbenzene, and crystallises in pale yellow needles, melting at $108-109^\circ$. None of these compounds smell of musk.
J. B. T.

Dinitrobutyltoluene. By A. BAUR (*Ber.*, 27, 1624).—In a previous communication on artificial musk (Abstr., 1891, 1464), dinitrobutyltoluene was described as a viscid liquid. After several months it has crystallised in small, pale yellow needles melting at 92° .
J. B. T.

Bromobutyltoluene. By A. BAUR (*Ber.*, 27, 1619—1623).—*Bromobutyltoluene*, $C_6H_5 \cdot C_4H_8BrMe$ [Me: C_6H_5 : Br = 1:3:6], is prepared by the action of bromine on butyltoluenesulphonic acid, or on the sodium salt at $50-60^\circ$; it is an almost colourless liquid, boiling at $240-242^\circ$, and has an aromatic smell. The *dinitro-derivative* is liquid, has a characteristic pungent odour, and could not be converted into a trinitro-compound. By the action of bromine on butyltoluene a

bromo-derivative is formed, which boils at 238—242°, and may be identical with the bromobutyltoluene prepared from the sulphonic acid. On treatment with nitric acid, two compounds are formed, the one, $C_6H_5 \cdot C_4H_2BrMe \cdot NO_2$, is a pale yellow liquid which volatilises with steam, readily decomposes when distilled, and darkens on exposure to air. The second, $C_6H_5 \cdot C_4HBrMe(NO_2)_2$, crystallises from alcohol in yellow needles melting at 107—108°. Neither of these substances smells of musk. By the action of bromine on butyltoluenesulphonic acids, or the sodium salt, at 20—30° the *bromo-sulphonic acid* is formed and crystallises in colourless, lustrous plates. The *sodium* and *lead salts* are crystalline. On treatment with nitric acid, it is converted into trinitrobutyltoluene and *butyltoluenenitro-bromosulphonic acid*, which is soluble in water and is being further investigated.

J. B. T.

Bye-Products formed in the Preparation of Butyltoluene.

By A. BAUR (*Ber.*, 27, 1606—1609).—An examination of the various fractions obtained during the purification of butyltoluene (*Abstr.*, 1891, 1464), shows that the portion boiling at 160—180° consists chiefly of butylbenzene (b. p. 167°).

The fraction 180—190° contains a little butylxylene, although the greater portion is butyltoluene; butylxylene is also contained in the fractions 190—200° and 200—218°. Tertiary butylxylene, which boils at 202°, is readily sulphonated; the *sodium salt* crystallises in lustrous plates, the sulphonamide in pearly plates melting at 141—142°, whilst the sulphanilide forms colourless needles melting at 143—144°.

The fraction 220—250° contains two hydrocarbons; the one is tertiary dibutylbenzene, and crystallises in colourless prisms melting at 76°; the *dinitro-derivative*, $C_{14}H_{20}(NO_2)_2$, crystallises in colourless needles, melts at 167—168°, and has a faint odour of musk. A trinitro-compound could not be obtained. *Barium dibutylbenzenesulphonate*, $2(C_{14}H_{21}SO_3)_2Ba + 7H_2O$, crystallises in colourless plates. The liquid hydrocarbon boils at 240—245°, and is *dibutyltoluene*; the *trinitro-derivative*, $C_{15}H_{21}(NO_2)_3$, crystallises in colourless plates, melts at 152—153°, and has a faint odour of musk. Both dibutylbenzene and dibutyltoluene were prepared, for purposes of comparison, directly from benzene, isobutylic bromide or pseudobutylic chloride, and aluminium chloride.

The fraction boiling above 250° after purification appears to consist of tributylbenzene and tributyltoluene, and is being further investigated.

J. B. T.

Ethylbutylbenzene. By A. BAUR (*Ber.*, 27, 1611—1614).—Ethylbutylbenzene is readily prepared by the action of ferric chloride on a mixture of pseudobutylic chloride and ethylbenzene at about 10°; it boils at 205—206°, and the yield is 73 grams from 200 grams of ethylbenzene. At higher temperatures or in presence of aluminium chloride the reaction is much more complicated. *Sodium ethylbutylbenzenesulphonate* crystallises in colourless, lustrous plates. The *sulphonamide*, $C_{12}H_{17}SO_2NH_2$, is deposited from alcohol in plates melting at

98°. The *disulphonamide*, $C_{13}H_{16}(SO_2NH_2)_2$, and the *disulphonic chloride* are crystalline, the former melts at 228—229°. The *dinitro-derivative*, $C_{13}H_{16}(NO_2)_2$, crystallises in pale yellow needles, melts at 140°, and has a faint odour of musk. The *trinitro-product* was only obtained on one occasion; it smells strongly of musk, is readily soluble in alcohol, and crystallises with difficulty. J. B. T.

Stability of Iodoso-compounds at Ordinary Temperatures.

By C. WILLGERODT (*Ber.*, 27, 1826—1827).—A sample of iodosobenzene, after being at the Chicago Exhibition, appeared unchanged, but, on treatment with chloroform, proved to have decomposed completely into iodobenzene and iodoxybenzene; another specimen which had been kept on paper, under a watch-glass, for about a year, became white and decomposed in a similar manner. Under the same conditions, metanitroiodosobenzene and orthochloriodosobenzene were completely decomposed into the corresponding iodoxy- and iodo-derivatives; parabromiodosobenzene was scarcely changed, whilst parachloriodobenzene acetate was converted into the iodoso-compound. J. B. T.

Iodoso- and Iodoxy-derivatives of Paradiiodobenzene. By C. WILLGERODT (*Ber.*, 27, 1790—1794).—*Diiodobenzene dichloride*, $C_6H_4I_2Cl_2$, is obtained by passing chlorine into a chloroform solution of paradiiodobenzene, until a considerable quantity of the dichloride is precipitated. It crystallises in beautiful, short, yellow prisms, and decomposes at 150°. When dissolved in alcohol, acetone, or acetic acid it is completely decomposed into paradiiodobenzene.

Paraiodosoiodobenzene, $C_6H_4I \cdot IO$, obtained by treating the dichloride with sodium hydroxide, is an amorphous, bright, yellow powder, and explodes at 120°. When boiled with water, it is converted into iodoxyiodobenzene and paraiodobenzene, and when boiled with alcohol into paraiodobenzene.

Paraiodophenyliodoacetate, $C_6H_4I \cdot I(OAc)_2$, is obtained by rubbing the preceding compound with cold acetic acid. It crystallises in transparent plates, and melts at 215°. When paraiodosoiodobenzene is dissolved in boiling acetic acid, paradiiodobenzene, the acetate, and a compound which melts at 210—225° are obtained; the latter is probably impure paradiiodosobenzene.

Paraioxyiodobenzene, $C_6H_4I \cdot IO_2$, is obtained, either by boiling iodosoiodobenzene with water, or by heating it in a current of steam at 90—100°. It crystallises in white needles, and explodes with a loud report at 232°.

Diiodobenzene tetrachloride, $C_6H_4(ICI_2)_2$, is obtained in a pure state from paradiiodobenzene dichloride and chlorine. It crystallises in bright, yellow needles, and decomposes at 157—159° (*Abstr.*, 1893, i, 149).

Paradiiodosobenzene, isomeric with iodoxyiodobenzene, is a bright, yellow powder, and when heated decomposes without explosion.

Paraphenylene diiodide tetracetate, $C_6H_4[I(OAc)_2]_2$, is obtained by boiling the preceding compound with acetic acid. It crystallises in small prisms, and decomposes and melts at 232°.

Paradiiodoxybenzene, $C_6H_4(IO_2)_2$, is obtained by boiling diiodosobenzene with water. It crystallises in white, microscopic needles.

E. C. R.

Diphenylic Selenide and its Derivatives. By F. KRAFFT and R. E. LYONS (*Ber.*, 27, 1761—1768; Abstr., 1894, i, 88).—Diphenylic selenide, obtained by the method already described by the author), boils at 159° under 10 mm., at 163° under 14 mm., at 167° under 16.5 mm., at 199° under 55 mm., at 219° under 100 mm., and at 227° under 126 mm. pressure. It is decomposed when heated with strong nitric acid, but dissolves in cold nitric acid (sp. gr. = 1.4) to form the nitrate of diphenylic selenoxide, which, on the addition of hydrochloric acid, is converted into the dichloride, Ph_2SeCl_2 (m. p. 182°).

Diphenylic diselenide, Se_2Ph_4 , is obtained from diphenylic selenide by a method similar to that by which phenylic disulphide is obtained from phenylic sulphide, namely, by warming the selenide with selenium. It crystallises in yellow needles, melts at 63.5° , and distils at 202 — 203° under 11 mm. pressure, with slight decomposition. When distilled under the ordinary pressure, either alone or dissolved in alcohol, it is decomposed into phenylic selenide and selenium.

Phenylic hydroselenide, $SeHPh$, is obtained by reducing the diselenide with sodium and alcohol, acidifying the product with sulphuric acid, and subjecting it to steam distillation. It is a colourless, highly refractive oil, boils at 183° , and oxidises, on exposure to air, to form the diselenide. The specific gravity at $0^\circ = 1.5057$, at $15^\circ = 1.4865$. It gives yellowish-red, unstable precipitates with alcoholic silver and lead solutions.

Dichlorophenylic selenide, $Se(C_6H_4Cl)_2$, is obtained, together with phenyl selenide, by heating the dichloride, Ph_2SeCl_2 , first at 140 — 150° , and then at 170 — 180° . It crystallises in lustrous leaflets, and melts at 95 — 96° .

Dibromophenylic selenide, $Se(C_6H_4Br)_2$, is obtained in a similar way to the chloro-compound, or by heating diphenylic selenide with bromine at 140° . It crystallises in lustrous, hexagonal leaflets, and melts at 115.5° .

β -Dinaphthyllic selenide, $Se(C_{10}H_7)_2$, is obtained by heating β -dinaphthylsulphone with selenium. It boils at 298° under 12 mm. pressure, melts at 138.5° , and forms with bromine the orange-red dibromide, $SeBr_2(C_{10}H_7)_2$, which when treated with alkalis is reconverted into the selenide.

E. C. R.

Diphenylic Telluride and the Preparation of Sulphides, Selenides, and Tellurides. By F. KRAFFT and R. E. LYONS (*Ber.*, 27, 1768—1773).—When mercury diphenyl, $HgPh_2$, is heated with tellurium dichloride at 220 — 225° , monochlorobenzene, and mercury telluride are formed.

Diphenylic telluride, $TePh_2$, is obtained by heating mercurodiphenyl with tellurium in an atmosphere of carbonic anhydride at 220° . It is a clear oil, which boils at 174° under 10 mm., and at 182 — 183° under 16.5 mm. pressure, whilst under ordinary pressures it decomposes,

yielding benzene and a crystalline solid. The sp. gr. at $0^{\circ} = 1.5741$, and at $15.2^{\circ} = 1.5558$.

Phenylic telluride dibromide, TeBr_2Ph_2 , is obtained by adding bromine to an ethereal solution of the telluride. It crystallises in small, lustrous prisms, melts at 203.5° , and is very similar to the selenium compound. When warmed with a solution of sodium hydroxide at 50° , it is converted into *phenylic telluroxide*, TePh_2O , which crystallises in needles, and melts at 185° with decomposition.

Mercury diphenyl, when heated with selenium and sulphur at 220 – 230° , is converted respectively into diphenylic selenide and sulphide. And this method is a very convenient one for the preparation of these and similar compounds.

Finally, the authors give tables showing the great similarity of the sulphur, selenium, and tellurium compounds. E. C. R.

Melting Points of some Phenols and their Benzoates. By A. BÉHAL and E. CHOAY (*Compt. rend.*, 118, 1211–1213).—The authors have prepared synthetically, by diazotisation of the corresponding amines, the phenols which, from their boiling point, might exist in officinal cresote. The benzoates were obtained by the action of benzoic chloride on a solution of the phenol in excess of sodium hydroxide solution. With the exception of the orthocresyl compound, which is liquid, the benzoates are all crystalline solids, very soluble in most organic solvents, but insoluble in water. The melting points and boiling points of the phenols were found to be as follows:—Phenol, m. p. 42.5 – 43 , b. p. 178.5° ; orthocresol, m. p. 30° , b. p. 178.5° ; metacresol, m. p. 4° , b. p. 200° ; paracresol, m. p. 36.5° , b. p. 199° ; orthoethylphenol (liquid), b. p. 202 – 203° ; metaethylphenol, m. p. -4° , b. p. 214° ; paraethylphenol, m. p. 45 – 46° , b. p. 218.5 – 219° ; ortho-xyleneol [$1:2:3$], m. p. 73° , b. p. 212 – 213° ; ortho-xyleneol [$1:2:4$], m. p. 65° ; b. p. 222° ; paraxyleneol, m. p. 75° , b. p. 208 – 209° ; metaxyleneol [$1:3:4$], m. p. 25° , b. p. 208 – 209° .

For the corresponding benzoates, the values are:—Phenyl, m. p. 69° , b. p. 298 – 299° ; orthocresyl (liquid), b. p. 307° ; metacresyl, m. p. 54° , b. p. 313 – 314° ; paracresyl, m. p. 71.5° , b. p. 315.5 – 316° ; orthoethylphenyl, m. p. 38° , b. p. 314 – 315° ; metaethylphenyl, m. p. 52° , b. p. 322 – 323° ; paraethylphenyl, m. p. 59 – 60° , b. p. 328° ; ortho-xylol [$1:2:3$], m. p. 58° , b. p. 326 – 327° ; ortho-xylol [$1:2:4$], m. p. 58.5° , b. p. 333° ; paraxylol, m. p. 61° , b. p. 318 – 319° ; metaxylol [$1:3:4$], m. p. 38.5° , b. p. 321° ; metaxylol [$1:3:5$], m. p. 24° , b. p. 326° .

In some cases, the results agree with, but in others they differ considerably from, those of previous observers. The authors have not yet succeeded in obtaining the metaxyleneol [$1:2:3$] and its derivatives described by Greving. C. H. B.

Phenols and Ethers of Butyltoluene. By A. BAUR (*Ber.*, 27, 1614–1619).—*Trinitrobutylorthocresol*, $\text{C}_4\text{H}_2\text{C}_6\text{Me}(\text{NO}_2)_3\text{OH}$, is prepared by the action of nitric acid on butylorthocresol (b. p. 235 – 237°) at low temperatures, and crystallises from alcohol in yellow needles melting at 85 – 86° . From the silver salt, which crystallises in brown needles, the methoxy-derivative, $\text{C}_4\text{H}_2\text{C}_6\text{Me}(\text{NO}_2)_3\text{OMe}$, was

obtained; this is deposited in yellowish needles, melts at 69—70°, and has an odour of musk. It is also formed by nitrating butyl-orthomethoxytoluene. That the above compounds contain a tertiary butyl group is shown by the preparation of the phenol, by the action of zinc chloride on a mixture of cresol and isobutylic alcohol or pseudo-butylic chloride; the same phenol is also formed on fusing sodium metabutyltoluenesulphonate with potash. Butylmetacresol and butylparacresol resemble the ortho-derivative, and boil at about the same temperature, the *nitro-compounds* crystallise with great difficulty, and have the odour of musk. The *methoxy-derivatives* are oily.

Butylmetamethoxytoluene, which boils at 222—224°, is nitrated with difficulty, as the butyl group is readily eliminated, and trinitromethoxytoluene formed. The propoxy- and amyloxy-compounds decompose in a similar manner. By the action of nitric acid on butylmetamethoxytoluene in glacial acetic acid solution at the ordinary temperature, a mixture of the *di-* and *trinitro-*compounds is formed; the former is oily and has a disagreeable odour, the latter crystallises in pale yellow plates, has an odour of musk, and darkens on exposure to light; the specimen was not quite pure. Attempts to determine the constitution of the butylmethoxytoluenes by oxidation with chromic anhydride or potassium permanganate were unsuccessful.

Butylmethoxybenzene, prepared by the action of aluminium chloride on methoxybenzene and isobutylic bromide or pseudobutylic chloride, has an aromatic odour, and boils at 220—222°. The *dinitro-derivative*, $C_6H_5 \cdot C_4H_9(NO_2)_2 \cdot OMe$, crystallises in lustrous, yellow plates, and melts at 100—101°. The *trinitro-derivative*, $C_6H_5 \cdot C_4H(NO_2)_3 \cdot OMe$, is deposited from alcohol in yellow needles melting at 74—75°. Neither of them has any odour of musk. J. B. T.

Preparation of Aniline. By A. WOHL (*Ber.*, 27, 1815—1818).—When writing his previous paper (this vol., i, 409), the author was unaware that in 1887 O. N. Witt suggested that in the preparation of naphthylamine ferrous chloride is the real reducing agent, and that the action takes place in accordance with the equations:—(I) $6FeCl_2 + C_{10}H_7NO_2 + H_2O = 3Fe_2Cl_4O + C_{10}H_7NH_2$; (II) $4Fe_2Cl_4O + 3Fe = Fe_3O_4 + 8FeCl_2$. Against this it is urged that the presence of other salts, such as calcium chloride, which have no reducing action, greatly facilitate the transference of oxygen from the nitro-compound to the iron, and that extremely concentrated solutions of ferrous salts, in absence of alkalis, have little action on nitrobenzene, and none, when the solutions are of the same strength as are employed technically. In the author's opinion the reduction is caused by the finely divided moist metal. Recently prepared ferric hydroxide, like basic ferric chloride, in presence of ferrous chloride, is converted into ferrosiferrous oxide by the action of finely-divided iron. Witt's second equation is, therefore, correct. In a footnote it is pointed out that dilute, aqueous solutions of nitrobenzene have a remarkably sweet taste. J. B. T.

Action of Ammonia and Primary Amines on Orthohydroxybenzylic Alcohol. By C. PAAL and H. SENNINGER (*Ber.*, 27, 1792—

1804).—Orthodihydroxybenzylamine is formed by the interaction of orthohydroxybenzylic alcohol and alcoholic ammonia at 140–145°; the yield is 40–50 per cent. of the theoretical, and a considerable quantity of the unaltered alcohol may be recovered. The compound gives a reddish-brown coloration and precipitate with sodium nitrite in acid solution. The hydrochloride, $C_{14}H_{13}NO_2 \cdot HCl$, gives a violet colour with ferric chloride, and melts at 190° instead of 144° as stated by Emmerich. Hydroxysalicylamide melts at 156° instead of 145°. *Saliretasine*, $C_{13}H_{11}O_3N$, is obtained in small quantity with orthodihydroxybenzylamine, and is the sole product of the action at 180–200°; it forms intensely yellow crystals, is insoluble, and decomposes above 300° without melting. The base is not decomposed by heating with alcoholic hydrochloric acid, concentrated sulphuric acid, or fuming nitric acid. The *hydrochloride* is colourless and insoluble. Orthohydroxybenzylaniline is prepared by the action of aniline on orthohydroxybenzylic alcohol, and has been previously obtained by O. Fischer and Emmerich (*Annalen*, 241, 343); the *sodium salt*, $NHPh \cdot CH_2 \cdot C_6H_4 \cdot ONa$, crystallises in silky, lustrous needles, and readily dissociates. The *nitrosamine* is a reddish-yellow, viscid liquid, which decomposes spontaneously. The *acetyl derivative* crystallises in long, colourless plates, melting at 96°. Orthohydroxybenzylparatoluidine, $C_6H_4Me \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot OH$, is formed from paratoluidine and orthohydroxybenzylic alcohol. The yield is almost quantitative.

J. B. T.

Condensation Products of Aromatic Amines with Formaldehyde in Alkaline Solution. By C. ABERHARDT and A. WELTER (*Ber.*, 27, 1804–1815).—*Methylenediphenyldiimide*, $CH_2(NHPh)_2$, is prepared by the interaction of aniline, formaldehyde, and potassium hydroxide in alcoholic solution at 100°; the yield is almost quantitative. It is also formed from formanilide and formaldehyde, and from anhydroformaldehydeaniline and aniline, and is probably identical with a compound obtained by Lermontoff from methylenic iodide and aniline, and with one (m. p. 48–49°) obtained in small quantity about nine years ago by Pratesi from aniline and formaldehyde. The base crystallises in large, lustrous, quadratic plates, melts at 64–65°, and boils and slightly decomposes at about 209–210°. It volatilises with steam but at the same time decomposes; on boiling with alcohol, it is resolved into anhydroformaldehydeaniline and a polymeric compound which crystallises in quadratic plates, and melts at 192°. On boiling with dilute sulphuric acid, both compounds yield formaldehyde.

Methylenediorthotolyldiimide, $CH_2(NH \cdot C_6H_4Me)_2$, is prepared in a manner similar to the phenyl-derivative, and crystallises in colourless prismatic needles melting at 52°. Anhydroformaldehydeorthotoluidine is not an oil as Tollens states, but crystallises in lustrous plates, and melts at about 100°. *Methylenediparatolyldiimide* is obtained like the ortho-derivative, and crystallises in silvery, lustrous plates melting at 86°; it is comparatively stable, can be recrystallised from alcohol, and dissolves in dilute mineral acids. Anhydroformaldehydeparatoluidine exists in two modifications, melting at 123° and 207–209° respectively. The quantity of alkali employed has little

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influence on the above condensations; potash acts better than soda; ammonia has no action.

By the action of hydrochloric acid or of amine hydrochlorides, the above imides are converted into diamidodiphenylmethane-derivatives. Diamidodiphenylmethane is deposited from water in lustrous plates or needles, and from benzene in prisms, melting at 88—89°. The *hydrochloride* crystallises in needles, it melts and darkens above 285°, and in aqueous solution exhibits a yellowish-green fluorescence. The *diacetyl-derivative* is crystalline, and melts at 228°. The *sulphonic acid* resembles that of diamidodiorthotolylmethane (see below); the *barium*, *potassium*, and *sodium salts* are crystalline. In addition to the methods already described, *diamidodiorthotolylmethane*,



is formed by the action of hydrogen chloride on the diimide at -15° , also by heating methylenediphenyldiimide or methylenediparatolyl-diimide with orthotoluidine hydrochloride. The *acetyl-derivative* melts at 198° . The *nitro-derivative* is yellow and sparingly soluble. The *hydrochloride* forms lustrous needles, melting at 278° with decomposition. The *disulphonic acid*, $\text{C}_{16}\text{H}_{16}\text{N}_2(\text{SO}_3\text{H})_2$, crystallises in dark green, sparingly soluble needles. With nitrous acid, a blue coloration is obtained changing successively to reddish-violet and dirty brown; the reaction is extremely delicate. The *ammonium* and *potassium salts* are crystalline.

Diamidophenyltolylmethane, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, is prepared by heating a mixture of methylenediorthotolyl-diimide, aniline, and aniline hydrochloride in molecular proportion; it crystallises in lustrous plates, and melts at 129° . The *hydrochloride* and *sulphate* are readily soluble. *Diamidoditolylmethane*, $\text{CH}_2(\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2)_2[\text{Me}:\text{NH}_2:\text{CH}_2, = 1:4:5]$, is prepared from methylenediparatolyl-diimide and paratoluidine hydrochloride, and crystallises in colourless, silky needles, melting at 92° . The *sulphate* is readily soluble in water, and the *hydrochloride* sparingly so, with a yellowish-green fluorescence.

Dihydroxydiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{OH})_2$, is prepared from the diamido-compound by the diazo-reaction; it crystallises in lustrous plates or needles, and is readily soluble in alkalis. The *potassium salt* crystallises in needles. *Paradihydroxydiorthotolylmethane*, $\text{CH}_2(\text{C}_6\text{H}_4\text{Me}\cdot\text{OH})_2$, is prepared in a similar manner, and is deposited in lustrous needles or plates melting at 126° . The *alkali salts* are readily soluble.

Methylenediphenyldiimide is converted into pararosaniline by heating it with aniline hydrochloride and aniline in presence of iron and an oxidising agent. Methylenediorthotolyl-diimide acts in a similar manner yielding *triamidotritolylmethane*, which is crystalline, and melts and decomposes at $155-160^\circ$. The *triacetyl-derivative* crystallises in small needles, melting at 170° . *Triamidotriorthotolyl carbinol hydrochloride* forms long, green needles, and is tolerably stable towards acids.

J. B. T.

Properties and Hydrolysis of Isomeric Amidines. By H. v. PECHMANN (*Ber.*, 27, 1699—1702).—*Benzenylphenylamidoparatolyl-*

imidine, $\text{NHP} \cdot \text{CPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$, was prepared by acting on benzoparatoluidide with phosphoric chloride, and treating the product with aniline; it melts at 133° . *Benzenylparatolylamidophenylimidine*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CPh} \cdot \text{NPh}$, obtained by the successive action of phosphoric chloride and paratoluidine on benzanilide, melts at 128° . These two substances cannot be distinguished from each other in appearance, and, when hydrolysed by boiling with water or dilute acid, the first does not yield, as would be expected, a mixture of benzanilide and paratoluidine, nor the second a mixture of benzoparatoluidide and aniline; but each yields a mixture of all these four substances. It may be supposed that a molecule of water is first taken up, and that the compound thus formed decomposes in two different ways.

C. F. B.

Action of Nascent Bromine on Benzene Derivatives. By W. VAUBEL (*J. pr. Chem.*, [2], 49, 540—545).—The author reviews the action of bromine on azobenzene, hydrazobenzene, diazobenzene, phenylhydrazine, acetylphenylhydrazine, benzamide, benzoic acid and its nitro-derivatives, and discusses the influence which the characteristic groups of these compounds exert on the position assumed by the bromine entering into the compounds (compare *Abstr.*, 1893, i, 560; this vol., i, 19).

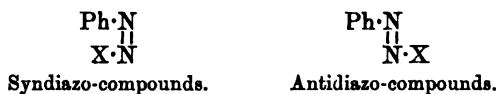
A. G. R.

Stereoisomerism of the Diazo-compounds; Constitution of Isodiazo-compounds. By A. HANTZSCH (*Ber.*, 27, 1702—1725; compare the two following abstracts).—The isodiazo-compounds have hitherto been regarded as structurally isomeric with the diazo-compounds, the iso-compounds being looked on as nitrosamines, such as isodiazo benzene, $\text{NHP} \cdot \text{NO}$. The evidence on which this formula principally rests is the fact that when the potassium salts of the isodiazo-compounds are treated with alkyl iodides, the nitrosamines of the secondary bases are produced, isodiazo benzene and methylic iodide, for example, yielding methylphenylnitrosamine, identical with that obtained from methylaniline. Against this view may be urged that the silver salts, on the other hand, yield chiefly the oxygen ethers, such as nitrodiazobenzene methyl ether, $\text{C}_6\text{H}_4\text{NO}_2 \cdot \text{N} \cdot \text{N} \cdot \text{OMe}$, and that the acid derivatives of the isodiazo-compounds, when hydrolysed in alkaline solution, yield true diazo-compounds, in spite of the fact that it is precisely in alkaline solution that the iso-compounds are most stable. The formation of "nitrogen"- or "oxygen"-ethers by the action of alkyl iodides on metallic derivatives cannot be used as evidence for the constitution of a compound, as is shown by the well-known case of the stereoisomeric oximes, and all that can be legitimately concluded from these facts is, that the diazo-compounds are tautomeric and may react either in the sense of a true diazo-compound or of a nitrosamine. That the diazo- and isodiazo-compounds have the same structural formula is proved by the following facts:—Two isomeric diazoamidobenzenes exist, and the structure of these cannot be explained by the nitrosamine formula. The newly discovered isomeride, which will form the subject of a separate communication, differs from the one already known in being explosive and in possessing the property of forming colouring matters directly.

If the nitrosamine formula were accepted, these isomeric substances would have the formulæ (1) $\text{NPh}\cdot\text{N}\cdot\text{NHPh}$ derived from $\text{NPh}\cdot\text{N}\cdot\text{OH}$, and (2) $\text{NHPh}\cdot\text{N}\cdot\text{NPh}$ derived from $\text{NHPh}\cdot\text{NO}$, and it will be seen that these formulæ are not different but identical.

Further (see the following abstract) the salts of benzenediazo-sulphonic acid exist in two isomeric forms, one of which passes spontaneously into the other in aqueous solution, a change which would necessitate a complex intramolecular change were the nitrosamine formula to be accepted.

The actual relation between the diazo- and isodiazocompounds can in fact only be consistently expressed by regarding these substances as stereochemically isomeric, in the same manner as the isomeric oximes. These substances will then be represented by the formulæ



which differ from the formulæ of the oximes only by the substitution of N for the group CH.

Such diazo-compounds as exist in the form of rings, due to the formation of inner anhydrides (as, for example, the anhydrides of diazobenzensulphonic acid and of nitrodiazophenol) must be syn-compounds, and, as these, as well as all ordinary diazo-compounds, react with phenols to produce colouring matters, this property may be taken as characteristic of the syn-series. In alkaline solution, these syn-compounds gradually change into the anti-compounds, and these do not form azo-colouring matters. This is confirmed by the fact that the syn-compounds tend to decompose with evolution of nitrogen, whilst the anti-compounds yield two molecules, each containing one of the diazo-nitrogen atoms. These decompositions are quite in accordance with the corresponding changes of the stereo-isomeric oximes. Finally, the syn-compounds are characterised by a tendency to explode, which is absent from the anti-compounds.

Among the syn-diazo-compounds are comprised the diazo-salts, and a new diazoamidobenzene and potassium benzenediazosulphonate, whilst the "isodiazocompounds," the well-known diazoamido-compounds, and the stable potassium benzenediazosulphonate belong to the anti-series; antidiazo-salts of the mineral acids are not yet known. The replacement of X in a syn-diazo-compound of the

formula $\begin{array}{c} \text{Ph}\cdot\text{N} \\ || \\ \text{X}\cdot\text{N} \end{array}$ by a more positive group renders the compound less

stable, and more liable to spontaneous change into the corresponding anti-compound, whilst, inversely, when the group X of an anti-compound is replaced by a more negative group the compound tends to change into the syn-derivative. It must be remembered that syn-

diazobenzene corresponds with synbenz-anti-aldoxime, $\begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{H} \\ || \\ \text{HO}\cdot\text{N} \end{array}$, and

antidiazobenzene with antibenz-syn-aldoxime, $\begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{H} \\ || \\ \text{N}\cdot\text{OH} \end{array}$. The use of

the contracted terms anti-aldoxime and syn-aldoxime entirely destroys the analogy.
A. H.

Stereoisomeric Salts of Benzenediazosulphonic acid. By A. HANTZSCH (*Ber.*, 27, 1726—1729; compare foregoing abstract). The acid of the constitution $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{SO}_3\text{H}$, which is usually termed diazobenzenesulphonic acid, is more correctly designated as benzenediazosulphonic acid. Its salts exist in two stereoisomeric forms.

Potassium benzenesyndiazosulphonate, $\text{Ph}\cdot\overset{\text{N}}{\underset{\text{N}}{\text{N}}}\cdot\text{SO}_3\text{K}$, may be obtained by bringing a solution of diazobenzene nitrate into an ice-cold solution of neutral potassium sulphite containing an excess of potassium carbonate. The salt is precipitated as a reddish-yellow crystalline mass, which is rapidly collected, washed once or twice with ice-cold water, and then dried on a porous plate. It forms a deep orange-coloured mass of plates, containing $1\text{H}_2\text{O}$; it rapidly loses water in the air, and then immediately begins to decompose, the colour becoming brownish, and finally dark brown, and sulphurous anhydride being evolved. The salt very frequently takes fire and explodes as soon as it becomes dry. It can nevertheless be analysed by exposing it over phosphoric oxide for a few minutes. This salt is a true derivative of diazobenzene nitrate (syn-series), as is shown by the liability to decomposition and by the fact that phenol is formed when it is boiled with water, and that it reacts with alkaline solutions of phenols to form coloured azo-compounds.

Potassium benzeneantidiazosulphonate, $\text{Ph}\cdot\overset{\text{N}}{\underset{\text{N}}{\text{N}}}\cdot\text{SO}_3\text{K}$, is the salt which is familiar from the descriptions of Strecker, E. Fischer, and Paal. The clear, dark yellow solution of the syn-salt becomes much lighter at the ordinary temperature, and the anti-salt soon separates out in granular crystals. It is pale yellow, is much less soluble than the syn-compound, and does not react with phenols to form coloured substances. Boiling water apparently produces much less phenol than with the syn-salt. The two salts behave similarly to reducing agents, with the exception that the reduction of the syn-salt is always accompanied by a slight evolution of nitrogen, which is never the case with the anti-salt. The syn-compound, moreover, is always partially converted into resin by bromine water, whilst this does not occur with the anti-salt.

The other salts of benzenediazosulphonic acid also exist in two forms. Thus the *barium salt* of the syn-acid rapidly separates as a yellow microcrystalline powder, which forms a clear solution in hydrochloric acid, whilst barium chloride produces no precipitate in a solution of the potassium salt of the anti-acid. The *silver salt* of the anti-series crystallises remarkably finely, forming yellow lustrous needles. Salts of silver and lead produce white precipitates of the sulphites of the metals with a solution of the syn-potassium salt, diazobenzene nitrate being quantitatively regenerated according to the equation $\text{Ph}\cdot\text{N}_2\cdot\text{SO}_3\text{K} + 2\text{AgNO}_3 = \text{Ag}_2\text{SO}_3 + \text{KNO}_3 + \text{Ph}\cdot\text{N}_2\cdot\text{NO}_3$.

Copper sulphate only produces a green coloration with the anti-potassium salt, whilst with the syn-salt a rapid and apparently quantitative evolution of nitrogen is produced, so that this salt, like the other syn-derivatives, undergoes Sandmeyer's reaction.

A. H.

Constitution of Benzenediazoic acid. By A. HANTZSCH (*Ber.*, 27, 1729—1731).—Benzenediazoic acid (phenylnitramine), which is a derivative of isodiazobenzene, probably has the constitution $\text{Ph}\cdot\text{N} \begin{smallmatrix} \nearrow \text{O} \\ \text{N} - \text{OH} \end{smallmatrix}$, and is therefore to be looked upon as an oxidised antidiazo-

benzenehydrate. Like isodiazobenzene itself, it is a tautomeric substance, and sometimes acts as though it had the constitution $\text{Ph}\cdot\text{NH}\cdot\text{NO}$, assigned to it by Bamberger; this, for instance, is the case when the potassium salt is acted on with methylic iodide, the "nitrogen-ether" being the chief product, whereas the silver salt yields the "oxygen-ether."

Similar considerations hold for naphthalenediazoic acid.

A. H.

Mixed Formazyl-compounds. By H. v. PECHMANN (*Ber.*, 27, 1679—1693).—The formation of a formazyl-derivative by the action of a diazo-compound on a hydrazone is, to take a particular case, represented by the equation $\text{N}_2\text{HPh}\cdot\text{CHPh} + \text{OH}\cdot\text{N}_2\text{Ph} = \text{H}_2\text{O} + \text{N}_2\text{HPh}\cdot\text{CPh}\cdot\text{N}_2\text{Ph}$. Since the hydrogen of the imido-group in the hydrazone takes no part in the reaction, it might appear that formazyl-compounds could be equally well prepared from hydrazones in which some other group was substituted for this hydrogen. Curiously enough, this is not the case. Nor is this the only peculiarity of the hydrogen atom in question. Formazyl-compounds of the types $\text{N}_2\text{HX}\cdot\text{CR}\cdot\text{N}_2\text{Y}$ and $\text{N}_2\text{HY}\cdot\text{CR}\cdot\text{N}_2\text{X}$ ($\text{R} = \text{H}, \text{COOH}, \text{Ph}, \text{or } \text{N}_2\text{Ph}$), exhibit so close a similarity that it might be supposed that structurally they are not merely isomeric, but identical, the position of the hydrogen atom being immaterial. As a rule, two corresponding compounds of this type have precisely the same appearance, and identical, or nearly identical, melting points; and, in chemical reactions, each compound yields, not only the products that it would be expected to form, but also those that would be expected from the other, or, in one case, both compounds give the products that would be expected from one only of the two. However, the author, chiefly on the ground that isomeric mixed amidines exhibit the same similarity whilst their melting-points differ by as much as 5° (this vol., i, 452), considers that these compounds are truly isomeric, and that their anomalous chemical behaviour is due to the fact that each is partially converted into its isomeride by most chemical reagents. He sees a similar isomerism in the case of mixed diazo-amido-compounds of the types $\text{NHX}\cdot\text{N}\cdot\text{NY}$ and $\text{NHY}\cdot\text{N}\cdot\text{NX}$, and of mixed amidines of the types $\text{NHX}\cdot\text{CR}\cdot\text{NY}$ and $\text{NHY}\cdot\text{CR}\cdot\text{NX}$.

Ethylic h-phenyl-a-paratolylformazylformate (see Abstr., 1893, i, p. 85) was prepared from paradiazotoluene and the phenylhydrazone either of ethylic hydrogen mesoxalate, or of ethylic acetacetate; it is red, and melts at 85° . The acid, $\text{N}_2\text{HPh}\cdot\text{C}(\text{COOH})\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me}$, is

brownish-red, and melts at 164—165°. When treated with diazobenzene, it yields *benzeneazo-h-phenyl-a-paratolylformazyl*,



which can also be prepared from formazylformic acid and para-diazotoluene; it is red, with a bronze lustre, and melts at 174—175°.

Methylic h-paratolyl-a-phenylformazylformate was prepared from diazobenzene and the paratolylhydrazone of methylic acetoacetate (yellow needles, melting at 100°, prepared from paradiazotoluene and methylic acetoacetate); it is red, and melts at 98°. The acid,

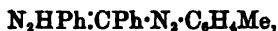


is red, and melts at 165—166°. When treated with diazobenzene, it yields *benzeneazo-h-paratolyl-a-phenylformazyl*,



which is red with a bronze lustre, and melts at 173—174°. It will be noticed that this compound and the acid from which it is derived melt at nearly the same temperatures as their isomerides mentioned above.

Formazylbenzene, $\text{N}_2\text{HPh}\cdot\text{CPh}\cdot\text{N}_2\text{Ph}$, is obtained by the action of diazobenzene on the phenylhydrazone of either benzaldehyde or glyoxylic acid; it is red with a greenish metallic lustre, and melts at 173·5°. *Diparatolylformazylbenzene*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\text{H}\cdot\text{CPh}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me}$, from paradiazotoluene and the paratolylhydrazone of benzaldehyde, is almost black with a greenish lustre, and melts at 166°. Like it in appearance is *h-phenyl-a-paratolylformazylbenzene*,



from paradiazotoluene and the phenylhydrazone of benzaldehyde; this melts at 155·5°, and also strongly resembles *h-paratolyl-a-phenylformazylbenzene*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\text{H}\cdot\text{CPh}\cdot\text{N}_2\text{Ph}$, melting at 155°, from diazobenzene and the paratolylhydrazone of benzaldehyde. When formazylbenzene is heated with sulphuric acid, in the presence of

acetic acid, aniline and *phenophenyltriazine*, $\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{N}\cdot\text{N} \\ \text{N}\cdot\text{O} \end{smallmatrix}\text{Ph}$, are formed;

the latter is yellow, and melts at 123°. Similarly *h-phenyl-a-paratolylformazylbenzene* yields aniline and *methylphenophenyltriazine*,

$\text{C}_6\text{H}_4\text{Me}\cdot\begin{smallmatrix} \text{N}\cdot\text{N} \\ \text{N}\cdot\text{O} \end{smallmatrix}\text{Ph}$, which is yellow, and melts at 95—96°. Curiously

enough, *h-paratolyl-a-phenylformazylbenzene* yields the same products, and not, as would be expected, paratoluidine and phenophenyltriazine.

C. F. B.

Decomposition-products of Formazyl-compounds. By H. v. PECHMANN and P. RUNGE (*Ber.*, 27, 1693—1699; compare the first paragraph of the preceding abstract).—A number of formazyl-compounds have been reduced with zinc-dust and sulphuric acid in the presence of alcohol. Two atoms of hydrogen are taken up, and the substance formed, reacting with a molecule of water, splits up into a mixture of hydrazine and hydrazide. But formazyl-compounds of

the type $N_2HX:CR:N_2Y$ do not yield only the products which would be expected, as the result of the changes



they also yield the hydrazine, N_2H_2Y , and the hydrazide, $CRO:N_2H_2X$, which would be expected, as the products of the reduction of the isomeric formazyl-compound $N_2HY:CR:N_2X$. This anomaly might be explained by supposing the substance $N_2HX:CR:N_2H_2Y$ to form, with a molecule of water, a compound that afterwards decomposes in two different ways. This anomalous reaction is exhibited by *h*-phenyl-*a*-paratolylformazylbenzene. Formazyl hydride itself, of course, gives normal products, as here the groups X and Y are identical; both = Ph. Those compounds, in which the imido-nitrogen atom is replaced, can, of course, give only one hydrazine and one hydrazide on reduction. Thus acetylformazylhydride, $N_2AcPh:CH:N_2Ph$, yields only *as*-acetylphenylhydrazine, N_2H_2AcPh , and *s*-formylphenylhydrazine, $CHO:N_2H_2Ph$. And the two isomerides, *h*-acetylphenyl-*a*-paratolylformazylhydride, $N_2AcPh:CH:N_2C_6H_4Me$ (orange-yellow prisms melting at 157.5°), and *h*-acetylparatolyl-*a*-phenylformazylhydride,



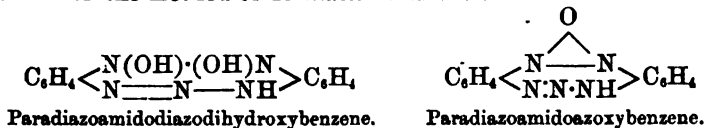
(yellow needles melting at 161°), a mixture of which is obtained by heating *either* of the two phenylparatolylformazylformic acids (see preceding abstract) with acetic anhydride, yield, the first *as*-acetylphenylhydrazine and *s*-formylparatolylhydrazine, the second *as*-acetylparatolylhydrazine and *s*-formylphenylhydrazine. And these two isomerides, further, on hydrolysis yield respectively *h*-phenyl-*a*-paratolylformazylhydride, $N_2HPh:CH:N_2T$, and *h*-paratolyl-*a*-phenylformazyl, $N_2HT:CH:N_2Ph$; these cannot be distinguished from each other, for both form ruby-red plates, both melt at 116 – 117° , and both, when treated with acetic anhydride, yield the same mixture of the two isomeric acetic derivatives mentioned above. C. F. B.

Reduction of Paradinitrodiazoamidobenzene. By B. PAWLEWSKI (*Ber.*, **27**, 1565–1568).—Paradinitrodiazoamidobenzene is best prepared by adding an excess of amyl nitrite to a solution of paranitrilaniline in ethylic acetate. The pure substance melts at 231° (stated as 223° by Meldola and Streatfield, *Trans.*, 1886, 626). The reduction of this substance has been carried out by these two chemists, who observed the production of a magenta-red coloration, but only obtained paraphenylenediamine. The author has obtained three distinct products, the third of which will form the subject of a separate communication.

(1.) When the dinitro-compound is heated with weak alcoholic potash or alcoholic sodium ethoxide, a dark coloured powder is formed which may be purified by dissolving it in ethylic acetate and precipitating with alcohol. It then forms a brick-red powder of the composition $C_{12}H_{11}N_3O_2$, melts and decomposes at 225 – 227° , and is sparingly soluble; its solutions in methylic alcohol, ethylic acetate, and alcohol are yellow, and give a magenta-red coloration with potash, which disappears on acidification.

(2.) When this solution or paradinitrodiazoamidobenzene itself is boiled with concentrated alcoholic potash, an amorphous, reddish-brown precipitate is formed which has the composition $C_{11}H_8N_8O$, decomposes without melting at $255-260^\circ$, and gives red solutions in methylic alcohol, acetone, and ethylic acetate.

The author ascribes the following formulæ to these compounds on account of the method of formation and their relation to each other.



A. H.

Stereoisomeric Diazoamido-compounds. By A. HANTZSCH (*Ber.*, 27, 1857—1866; compare this vol., i, 455).—The substances usually termed diazoamido-compounds may be more conveniently termed benzenediazoamides, anilides, &c., ordinary diazoamidobenzene being, for example, benzeneantidiazooanilide.

Benzenesyndiazooanilide, $\begin{array}{c} \text{Ph} \cdot \text{N} \\ \parallel \\ \text{NHPh} \cdot \text{N} \end{array}$, is formed when an alcoholic solution of pure diazobenzene chloride is treated in the cold with a solution of sodium methoxide in methylic alcohol, or when a concentrated aqueous solution of diazobenzene chloride, prepared from the pure crystalline chloride, is brought into a concentrated solution of sodium carbonate which contains some of the solid carbonate. It is also formed in the pure state when a mixture of diazobenzene chloride and aniline hydrochloride in exactly molecular proportion is dissolved in a little water and treated in the same manner. The requisite mixture is best obtained by the decomposition of ordinary diazoamidobenzene with hydrogen chloride, since, if the exact proportions be not employed, the product always contains more or less of the ordinary (anti)diazooamidobenzene. The nature of the action which occurs in this preparation has not yet been ascertained. Benzenesyndiazooanilide is a pale yellow, microcrystalline powder, which is insoluble in water, sparingly soluble in alcohol, readily in ether, very readily in benzene. The solutions readily undergo decomposition, nitrogen being evolved, and a resinous substance formed. When the pure substance is kept, it slowly becomes dark coloured, and changes into a viscid mass. It deflagrates brilliantly when heated to 75° , explodes feebly when brought into concentrated sulphuric acid, and sometimes explodes spontaneously when exposed to sunlight.

Paratoluenesyndiazotoluidide, $\begin{array}{c} \text{C}_6\text{H}_4\text{Me} \cdot \text{N} \\ \parallel \\ \text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{N} \end{array}$, is best prepared from paradiatzotoluene chloride and sodium carbonate or methoxide, the action of sodium carbonate on a molecular mixture of diazotoluene chloride and toluidine hydrochloride always giving rise to a mixture of the two isomerides. It closely resembles the benzene compound but is more stable, decomposing when heated at 78° , and not exploding in the sunlight.

Parabromobenzenesyndiazobromanilide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}^{\text{II}}\cdot\text{N}^{\text{I}}$, is formed as a light yellow powder when an ordinary diazotised solution of parabromaniline is brought into an excess of saturated aqueous sodium carbonate. It explodes readily when gently rubbed, and has not yet been closely examined.

All these syn-compounds are decomposed in ethereal solution by hydrogen chloride, a diazo-salt and the hydrochloride of the corresponding base being formed, so that they are structurally diazo-compounds, and do not possess a different structural form such as $\text{PhN} < \begin{smallmatrix} \text{N}^{\text{Ph}} \\ \text{NH} \end{smallmatrix}$. They also, like all the derivatives of the syn-diazo-series, have the power of combining directly with phenols to form colouring matters. This is best shown by covering the syn-diazoanilide with alcohol or acetone, and adding a solution of β -naphthol in soda containing as little free alkali as possible. A deep coloration is produced, whereas the ordinary anti-diazoanilides give no trace of a colouring matter when treated in this way. When benzenesyndiazoanilide is dissolved in alcoholic ammonia in the cold, and the solution evaporated after some time, benzeneantidiazoanilide is deposited along with a very small amount of resin. Alcoholic soda produces the same change, but rather more resin. The toluene compound undergoes the change even more readily than the benzene derivative. The behaviour of these compounds, then, confirms the general rule that the anti-compounds are stable in alkaline solutions. All the aromatic and mixed diazoamido-compounds previously prepared belong to the anti-series.

It is possible that in some cases the diazoamido-compounds are tautomeric; thus benzenediazotoluidide, $\text{NPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, may react as though it had the tautomeric formula, $\text{NHPh}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, which is identical with the formula of toluenediazoanilide, and this may account for the fact that the diazoamido-compounds, prepared from diazobenzene and toluidine and from diazotoluene and aniline, are apparently identical.

A. H.

Possible Stereoisomerism of Ethers of Metachloroquinone-oxime. By F. KEHRMANN (*Annalen*, 279, 27—39).—As stated by Bridge (this vol., i, 25), two isomeric benzoyl derivatives are obtained from metachloroquinoneoxime; but the statement of this chemist that this is due to the non-homogeneity of the oxime is erroneous. As a matter of fact, the author shows that both these benzoyl derivatives, which melt at 192° and 162° respectively, are converted into metachloroquinoneoxime (m. p. 141°) when heated with dilute soda. Both benzoyl derivatives, when treated successively with alkali and nitric acid, are converted into orthochlororthoparadinitrophenol (m. p. 112 — 113°); and when treated first with alkali and subsequently with stannous chloride and hydrochloric acid, they each yield chloroparamidophenol (m. p. 151 — 152°). When either of the benzoyl derivatives is hydrolysed with alkali, and the product reconverted into the benzoyl derivative, this proves in each instance to be a mixture

consisting principally of the higher melting compound. The author regards it most probable that the two benzoyl derivatives are stereoisomerides.

When chloroquinone is treated with α -methylhydroxylamine hydrochloride, and the product is crystallised from light petroleum, a chloroquinonemethoxime, crystallising in needles and melting at 122—123°, is obtained (compare Bridge, *loc. cit.*). A small quantity of an isomeride, crystallising in prisms and melting at 114—115°, was also isolated. The author has, however, not succeeded in obtaining the chloroquinonemethoxime (m. p. 97°) described by Bridge, but he finds that when the isomerides mentioned above are fused and allowed to resolidify, the melting point of both is 97°. The isomerides may be recrystallised unchanged from hot nitric acid of sp. gr. 1.4, but are readily converted into orthochloroparamidophenol on treatment with stannous chloride and hydrochloric acid, a fact which proves that they are structurally identical.

The author is engaged on further experiments; he states that he has succeeded in preparing metachloroquinoneoxime in a state of purity by means of the acetyl derivative, which latter also exists in two modifications.

A. R. L.

Dinitrophenyl Ethers of Oximes. By A. WERNER (*Ber.*, 27, 1654—1657).—The *dinitrophenyl ethers* of the following oximes were prepared; the method adopted was to mix the oxime (1 mol.) with sodium ethoxide (1 mol.), and then add 1 : 2 : 4-chlorodinitrobenzene, when the desired compound crystallised out. These ethers on hydrolysis generally yield dinitrophenol; they could not be made to yield the dinitrophenyl ether of hydroxylamine. The formulæ, melting points, and colour, if any, of the ethers prepared are given below against the names of the oximes from which they are respectively derived; R stands for the group $-C_6H_3(NO_2)_2$. *Antibenzaldoxime*, $CHPh.NOR$, 139—140°, yellow; *antimetanitrobenzaldoxime*, $NO_2.C_6H_4.CH.NOR$, 188°; *benzenylamidoxime*, $NH_2.CPh.NOR$, 181°, yellow; *acetoxime*, $CM_2.NOR$, 90°; *antiethylbenzhydroximic acid*, $OEt.CPh.NOR$, 150—152°; *menthoneoxime*, $C_{10}H_{18}.NOR$; *lævo-rotatory*, 112°; *dextro-rotatory*, 72°.

C. F. B.

The Iodonium Bases. By C. HAETMANN and V. MEYER (*Ber.*, 27, 1592—1599; compare this vol., i, 242).—*Diphenyliodonium nitrate*, $IPh_2.NO_3$, is obtained as a white crystalline precipitate, when a strong solution of the base is neutralised with concentrated nitric acid. It dissolves very readily in hot water and separates on cooling in small plates or compact spear-shaped crystals. It melts at 153—154°, forming a clear liquid which soon decomposes, whilst if a larger quantity of it is heated it explodes gently. This salt may also be obtained by dissolving the chloride in fuming nitric acid.

Diphenyliodonium hydrogen sulphate, $IPh_2.HSO_4$, is so readily soluble that it cannot be recrystallised from water, but may be purified by precipitating its alcoholic solution with ether. It has

an acid reaction, melts at 153—154°, and decomposes at a somewhat higher temperature.

Diphenyliodonium acetate, $\text{IPh}_2\cdot\text{OAc}$, is best prepared by shaking iodoxybenzene with aqueous soda, acidifying with acetic acid, filtering and cooling the filtrate. The acetate melts and decomposes at 120°, and cannot be recrystallised from water. It gives up the whole of its acetic acid when distilled in a current of steam.

Diphenyliodonium periodide, $\text{IPh}_2\cdot\text{I}_3$. Like the alkylammonium iodides, phenyliodonium iodide forms a crystalline additive compound with iodine. It is prepared by grinding the iodide with alcoholic iodine, crystallises from alcohol in almost black needles, with a diamond lustre, and melts at 138°.

Diphenyliodonium mercurichloride, $\text{IPh}_2\cdot\text{HgCl}_2$, crystallises from water in white, very refractive needles, and melts and decomposes at 172—175°.

The *aurochloride*, $\text{IPh}_2\cdot\text{AuCl}_4$, which is almost insoluble in cold water, crystallises in golden-yellow needles and melts and decomposes at 134—135°. The *platinochloride*, $(\text{IPh}_2)_2\text{PtCl}_6$, is only sparingly soluble in hot water and crystallises in microscopic needles, melting and decomposing at 184—185°.

The analogy between the iodonium compounds and the salts of the heavy metals also extends to the sulphur compounds of the base. When yellow ammonium sulphide is added to a solution of the base, a thick, orange-red precipitate is produced, resembling antimony sulphide. This precipitate is stable at 0°, but at the ordinary temperature it undergoes rapid decomposition and yields a mobile oil which consists of moniodobenzene and a mixture of phenylic sulphides, mainly the trisulphide, Ph_2S_3 . The orange-red compound is, therefore, probably *diphenyliodonium trisulphide*, $(\text{IPh}_2)_2\text{S}_3$. The corresponding *monosulphide*, $(\text{IPh}_2)_2\text{S}$, is obtained as a pale yellow precipitate when sodium monosulphide is added to a solution of the base. It behaves in a similar manner to the trisulphide, yielding moniodobenzene and phenylic sulphide, Ph_2S .

When an aqueous solution of the free base is treated in the cold with 5 per cent. sodium amalgam, reduction takes place quantitatively according to the equation



When the iodide formed is boiled with aqueous soda it yields iodobenzene and phenol.

The preparation of the iodonium base by means of caustic soda gives a smaller yield (55—63 per cent.) than is obtained by the use of silver oxide (93 per cent.), but has the advantage that the iodic acid formed in the reaction dissolves in the liquid and on treatment with sulphurous acid yields exactly the amount of hydriodic acid required to react with the base, so that no potassium iodide need be added, and nearly all the iodine used is converted into the iodonium iodide. A small amount (3·5 per cent.) of the base is also formed in the preparation of iodoxybenzene from iodosobenzene by means of steam.

The physiological action of the chloride of the base resembles that

of ammonium salts, on the one hand, and of heavy metals such as lead and thallium on the other.

Doses of 0.02—0.03 gramme produce total paralysis in frogs, both the motor nerve endings and the muscle substance being affected. A dose of 0.08 per kilo. proves fatal to rabbits, the spinal chord and *medulla oblongata* being also affected. A. H.

The Law of Etherification of Aromatic acids. By V. MEYER and J. J. SUDBOROUGH (*Ber.*, 27, 1580—1592).—Benzoic acid and its substitution products as a rule yield 90 per cent. of an ethereal salt when treated with methylic alcohol and hydrochloric acid in the cold. The symmetrical trisubstitution products of benzoic acid, however, are an exception to this rule and yield no ethereal salt whatever under the same conditions. In some cases a small amount of ethereal salt is obtained from such compounds (this vol., i, 243), but this is due to impurities, and when these have once been removed by etherification, the purified acid yields no ethereal salt at all. This rule holds absolutely for all the 1:3:5-trisubstitution derivatives of benzoic acid (Me, NO₂, Br, and COOH) with which experiments have been made, except those containing one or more hydroxyl-groups. The same is true of all substituted benzoic acids in which the hydrogen atoms 2:6 [COOH = 1] have been replaced by other atoms or groups. Thus *tetrabromobenzoic acid* [COOH:Br₄ = 1:2:3:4:6] gives no ethereal salt under the conditions described above. This acid is prepared by means of the diazo-reaction from tribromometamidobenzoic acid and forms colourless needles, melting at 173—174°, which are sparingly soluble in hot water.

Tribromometamidobenzoic acid



and *nitrotetrabromobenzoic acid* [COOH:Br₄:NO₂ = 1:2:3:4:6:5] also give no ethereal salts. The latter of these acids is obtained by the nitration of the tetrabromo-acid described above, and forms colourless needles, melting at 235°.

2:4-Dibromobenzoic acid, on the other hand, yields 95 per cent. of ethereal salt. This acid is obtained from 2:4-dibromaniline by means of Sandmeyer's reaction; it forms slender needles and melts at 163—164°. Finally, *2:6-dibromobenzoic acid* yields no ethereal salt. This acid, which may be obtained from 2:6-dibromaniline in a similar manner to the foregoing, forms small needles melting at 136—137°.

The acids which do not yield ethereal salts when treated with alcohol and hydrochloric acid, can readily be converted into these substances by the action of methylic iodide on their silver salts.

The authors ascribe this remarkable behaviour to a stereochemical cause, the substituent groups being supposed by them to hinder the introduction of the alkyl group to such an extent that under the prescribed conditions the reaction does not proceed. Acids in which the carboxyl-group is connected with the benzene nucleus by means of an intermediary carbon atom readily undergo etherification. Thus *mesitylacetic acid*, C₆H₃Me₃CH₂COOH, yields 96 per cent. of

the *methyl*ic salt, which boils at 255—256°; and mesityl*glyoxylic* acid, $C_6H_3Me_3CO \cdot COOH$, behaves in a similar manner, the *methyl*ic salt boiling at 273—275°. This behaviour is quite in accordance with the stereochemical view of the phenomenon.

Among the derivatives of mellitic acid, the behaviour of pyromellitic acid $[(COOH)_4 = 1:2:4:5]$, prehnitic acid $[(COOH)_4 = 1:2:3:4]$ and mellitic acid (benzenehexacarboxylic acid) has been examined and found in exact accordance with the rule established above. Thus mellitic acid does not undergo etherification, prehnitic acid only yields a *dimethyl*ic salt (melting at 176—177°) and pyromellitic acid gives the tetramethylic salt. The constitution of a substituted benzoic acid may, therefore, be readily tested in this way and the method may also be used for purifying or isolating those acids which will not undergo etherification.

A. H.

Isomeric Nitrobenzoic acids. By ORCHSNER DE CONINCK (*Compt. rend.*, 118, 1104—1105 and 1207—1208).—The mean solubilities of the three nitrobenzoic acids in water are as follows: ortho-acid at 11.2°, $\alpha = 0.0533$, meta-acid at 11.9°, $\alpha = 0.0268$, par-acid at 12.2°, $\alpha = 0.0024$.

Orthonitrobenzoic acid is rapidly carbonised when gently heated with ordinary sulphuric acid, but the meta- and para-acids simply dissolve and at most become amber coloured. When heated with ordinary nitric acid, orthonitrobenzoic acid yields a colourless solution, the meta-acid a slightly yellow solution, and the para-acid dissolves only partially and yields a pale yellow solution. With fuming nitric acid the results are similar, but all three acids dissolve completely.

Warm aqua regia completely dissolves the ortho-acid and partially dissolves the meta- and para-acids, bright yellow solutions being formed.

The action of nitric acid and of aqua regia affords a ready means of distinguishing nitrobenzoic acids from amidobenzoic acids. A dilute aqueous solution of chromic acid likewise distinguishes the amido from the nitro-derivatives since it has no action on the latter below its boiling point.

All three nitrobenzoic acids are unaffected when exposed to sunlight in contact with dilute hydrochloric acid. When exposed in contact with dilute nitric acid, the meta-derivative slowly acquires a pale yellow coloration. When moderately concentrated solutions in acetone are exposed to sunlight, there is no change, but with dilute alcoholic solutions, the para-acid becomes bright yellow and the meta-acid pale yellow.

In all cases where there is any reaction at all, two of the nitrobenzoic acids behave similarly, whilst the third behaves differently from the other two.

C. H. B.

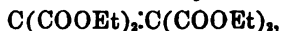
Formation of Ethereal Salts of Aromatic acids. By B. LEPSIUS (*Ber.*, 27, 1635).—Symmetrical trinitrobenzoic acid exemplifies V. Meyer's rule (this vol., i, 243); only 1.66 per cent. of methyl*ic* salt is formed.

C. F. B.

Preparation of Iodoxybenzoic acid. By C. HARTMANN and V. MEYER (*Ber.*, 27, 1600).—A more convenient method for the preparation of iodoxybenzoic acid than that originally described (Abstr., 1893, i, 577) is to dissolve 5.3 grams of iodosobenzoic acid in 4 grams of aqueous soda and saturate the cold solution with chlorine. After acidifying, the residue is extracted with ether to remove orthiodobenzoic acid, and the iodoxybenzoic acid is separated from unaltered iodosobenzoic acid as previously described. Iodoxybenzoic acid partially decomposes when kept, a large amount of it being converted into iodosobenzoic acid. A. H.

Sodium Borosalicylate. By P. ADAM (*Bull. Soc. Chim.*, [3], 11, 204—206).—It is well known that the solubility of salicylic acid in water is greatly increased by the addition of borax. On evaporating an aqueous solution containing sodium salicylate and boric acid in molecular proportion, a syrupy liquid is obtained, which slowly deposits *sodium borosalicylate*, $C_7H_5O_4BNa$, as a white, amorphous powder. It is soluble in 4 parts of cold water, and in methylic, ethylic, and amylalcohols, ethylic acetate, &c. Solutions of the salt do not give the reactions of boric acid; its alcoholic solution does not burn with the green flame characteristic of this acid. Borosalicylic acid does not seem to exist in the free state; on acidifying the solution of the sodium salt, boric and salicylic acids are deposited. W. J. P.

Action of Phenylhydrazine on Ethylic Benzalmalonate. By W. WISLICENUS (*Annalen*, 279, 23—26).—Wislicenus and Reitzenstein (this vol., i, 133) have shown that benzylidenediketohydrindene is decomposed by phenylhydrazine. The author now finds that when ethylic benzalmalonate, $CHPh(COOEt)_2$, is warmed with alcohol and phenylhydrazine for an hour, benzylidenephénylhydrazone and ethylic malonate are formed. The ethylic salt,



does not decompose in this manner when treated with phenylhydrazine. A. R. L.

Formation of Ethereal Salts of Chlorhydrin and of Dichlorhydrin. By C. GÖTTIG (*Ber.*, 27, 1602—1604).—The author has investigated the action of hydrogen chloride on a mixture of glycerol and various acids. Phthalic acid yields a product free from chlorine; gallic acid and succinic acid resemble the hydroxybenzoic acids (Abstr., 1892, 715), and give ethereal salts of dichlorhydrin, which have not been isolated. Paramethoxybenzoic acid yields an ethereal salt of dichlorhydrin; it crystallises in needles, melts at 74—76°, and is somewhat difficult to hydrolyse. As the compound is formed above 100°, it is probably a derivative of α -dichlorhydrin, and has the formula $OMe \cdot C_6H_4 \cdot CO \cdot OCH_2 \cdot CHCl \cdot CH_2Cl$. J. B. T.

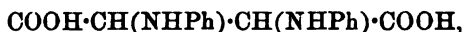
Acids from Benzoylacetonedicyanhydrin. By M. CARLSON (*Ber.*, 27, 1571—1574; compare Abstr., 1892, 1471).—The author has succeeded in obtaining larger amounts of the products of this reaction.

When crude benzoylacetonedicyanhydrin is dissolved in hydrochloric acid, and the liquid then saturated with hydrogen chloride, hydrocyanic acid is liberated, and an acid of the formula $C_{11}H_9O_3$ produced, along with acetophenone, and a large amount of resin. This acid forms colourless granules, and melts at 124—125°. It is monobasic, and yields an unstable, amorphous, *silver* salt, $C_{11}H_9AgO_3$. It is an unsaturated acid, and combines with 1 mol. of bromine, forming a *bromide*, $C_{11}H_7Br_2O_3$, which crystallises from light petroleum in colourless prisms, softens at 155°, and melts at 163°.

When the hydrolysis of crude benzoylacetonedicyanhydrin is carried out by means of boiling alcoholic potash, on the other hand, an isomeric acid, $C_{11}H_{11}O_3$, is produced. This crystallises in long needles, melts at 101—102°, and, like its isomeride, is very sparingly soluble in cold water. It is also a monobasic acid, and combines with 1 mol. of bromine to form a crystalline bromide. The constitution of these acids is being made the subject of further investigation.

A. H.

Aniline and Ethylic Isodibromosuccinate. By D. VORLÄNDER (*Ber.*, 27, 1604—1605).—Ethylic dianilidosuccinate,



is formed by the action of aniline on ethylic isodibromosuccinate in alcoholic solution. Attempts to convert the free acid into indigo by the action of dehydrating agents, such as fuming sulphuric acid, or phosphoric anhydride, were unsuccessful, but three times out of 40—50 experiments, indigo was produced by fusing the acid with potash, the necessary conditions for its formation, however, could not be determined.

J. B. T.

Application of Friedel and Crafts' Reaction to Thiophenol Ether. By K. AUWERS and C. BEGER (*Ber.*, 27, 1733—1741).—*Thioethylbenzophenone*, $SEt \cdot C_6H_4 \cdot C(Ph)_2$, is formed when thiophenyl ethyl ether is warmed in solution in carbon bisulphide with benzoic chloride and aluminium chloride. It forms lustrous, white prisms, which are sparingly soluble in light petroleum, and melt at 82—83°. When this ketone is treated with alkaline hydroxylamine solution, it yields a mixture of two stereochemically isomeric oximes, which may be separated by V. Meyer's method (*Annalen*, 264, 116).

Antithioethylbenzophenoneoxime crystallises from ethylic acetate in short compact, vitreous prisms, melting at 133—134°, and readily soluble in the usual solvents, with the exception of light petroleum. The *hydrochloride* is crystalline, and yields the original substance when decomposed with soda. The *acetate* forms compact, lustrous prisms melting at 99—100°. When the oxime is heated with alcohol, or an alcoholic solution of an alkali, it is partially converted into the isomeride of lower melting point. The constitution of the oxime is shown by the fact that when it is dissolved in ether and treated with phosphorus pentachloride, it is converted into *thioethylbenzanilide*, $SEt \cdot C_6H_4 \cdot C(OH) \cdot NPh$, which crystallises from alcohol in

snow-white plates with a satiny lustre, melting at 158°. This substance, when heated with hydrochloric acid, yields thioethylbenzoic acid, $\text{SEt}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, and aniline.

Synthioethylbenzophenoneoxime crystallises in slender needles, is slightly more soluble than the anti-compound, and, when heated, softens at 94°, and melts at 96°. Like its isomeride, it yields a crystalline hydrochloride, and is partially converted into the higher melting form by alcohol at 100°. The *acetate* forms slender needles melting at 58–60°. When treated with phosphorus pentachloride, this isomeride is converted into the *thioethylanilide of benzoic acid*, $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SEt}$, which melts at 145°, and when treated with hydrochloric acid yields benzoic acid and thioethylaniline,



the latter may be recognised by means of its *acetyl* derivative, $\text{SEt}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, which forms lustrous needles melting at 108–110°.

Thioethylacetophenone, $\text{SEt}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$, is obtained in a similar manner to the benzoyl derivative, and forms lustrous plates, which melt at 43·5°, and are slightly soluble in light petroleum. This ketone only yields one *oxime*, which crystallises in long, thin needles melting at 91°.

Thiophenyl ethyl ether also reacts with chloroformamide in the presence of aluminium chloride to form *thioethylbenzamide*,



which crystallises in broad, lustrous needles melting at 169–170°, *Thioethylbenzoic acid*, $\text{SEt}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, also forms broad, flat needles, and melts at 146°.

When phenylthiocarbimide is employed in this reaction, the *thioamylide of thioethylbenzoic acid*, $\text{SEt}\cdot\text{C}_6\text{H}_4\cdot\text{CS}\cdot\text{NHPh}$, is obtained; this forms golden-yellow, lustrous plates melting at 140–141°. When it is oxidised with potassium ferricyanide, it is converted into *thioethylbenzenylamidophenyl mercaptan*, $\text{SEt}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix}\text{C}_6\text{H}_4$, which forms white needles melting at 101–102°. A. H.

Constitution of the Rosanillines. By A. ROSENSTIEHL (*Bull. Soc. Chim.*, [3], 11, 212–213; compare *Abstr.*, 1893, i, 332).—A claim to priority as against Stock (*Abstr.*, 1893, i, 472).

W. J. P.

The Coloured and Colourless Derivatives of Di- and Tri-phenylmethane. By A. ROSENSTIEHL (*Bull. Soc. Chim.*, [3], 11, 213–216).—The author considers that V. Richter's and Noelting's rules respecting the colour of phenylmethane derivatives must be combined, in order to represent the facts. W. J. P.

Condensation of Aldehydes with α -Naphthaquinol and α -Naphthaquinone. By J. WURGAFT (*J. pr. Chem.*, [2], 49, 551–552).—By saturating a cold mixture of α -naphthaquinol (2 mols.) and benzaldehyde (1 mol.) with hydrogen chloride, red, rhombic

crystals of the compound $C_{27}H_{19}ClO_4 + H_2O$ are obtained. The crystals dissolve in alkalis yielding a blue solution, which slowly becomes brown. Since the same compound is obtained by the direct action of benzotrichloride on α -naphthaquinol in glacial acetic acid, it is inferred that this chlorine derivative is *tetrahydroxydinaphthylcarbinol chloride*; the dechlorinated carbinol, $OH \cdot CPh[C_{10}H_6(OH)_2]_2$, and its *acetyl*-derivative, which crystallises in white, rhombic tables, and melts at 246° , were prepared. A similar red colouring matter is obtained by a like treatment of a mixture of α -naphthaquinone with benzaldehyde.

A. G. B.

Butylnaphthalene. By A. BAUE (*Ber.*, 27, 1623).—Butylnaphthalene (b. p. 280°) is prepared from naphthalene, isobutylic bromide, and aluminium chloride, and is sparingly volatile with steam. The *trinitro*-derivative forms granular crystals, melts at 79 – 80° , with previous softening at about 50° , and has no odour of musk.

J. B. T.

Ketones from Pinene Derivatives. By L. C. URBAN and E. KREMERS (*Amer. Chem. J.*, 16, 404–406).—Nitrosopinene, whilst stable towards sulphuric acid, yields with hydrochloric acid a *ketone*, $C_{10}H_{14}O$, having a peppermint odour, and, therefore, probably a β -ketone.

L. T. T.

The Menthol Group. By L. C. URBAN and E. KREMERS (*Amer. Chem. J.*, 16, 395–404).—The rotation of menthene (*Abstr.*, 1892, 1479) is now given as $[\alpha]_D = +31.83^\circ$ (instead of $+26.40^\circ$), and of the nitrosochloride, melting at 113° , as $[\alpha]_D = +13.76^\circ$. An inactive nitrosochloride melting at 128° has also been obtained. *Menthene nitrosate*, $C_{10}H_{18}N_2O_4$, melts at 98° , and is optically inactive. *Menthene nitrosobenzylamine*, $NO \cdot C_{10}H_{18} \cdot NH \cdot C_6H_5$, from the nitrosate or nitrosochloride, melts at 107° , and is optically inactive. No piperidine base could be obtained, the alkaloid acting on the nitrosochloride like an alkali, and causing the separation of hydrogen chloride. *Nitroso-menthene*, produced by the action of alcoholic potash on the nitrosochloride or nitrate, yields, on sublimation, colourless needles, is volatile in steam, melts at 67° , and is optically inactive. On reduction, it yields an *amido*-compound, which, with the diazo-reaction, gives an unsaturated *secondary alcohol*, $C_{10}H_{18}O$, boiling at 210 – 215° . The amido-compound, which is, therefore, probably $C_{10}H_{17} \cdot NH_2$, rather than the saturated amine, $C_{10}H_{19} \cdot NH_2$, as anticipated, is being further investigated. In preparing the amine, small quantities of an *inactive menthene*, boiling at 204 – 206° , and volatile in steam, were produced. This yields an *oxime*, crystallising in needles, melting at 82° , and giving a crystalline hydrochloride. The menthene, on reduction by Beckmann's method, appears to give menthol, but the latter could not be fully identified. Nitrosomenthene is comparatively stable towards sulphuric acid, but with hydrochloric acid it yields an inactive *ketone*, $C_{10}H_{16}O$, a colourless oil of peppermint odour, boiling at 210 – 212° , and having a sp. gr. = 0.9150 at 20° . When the ketone is treated with hydroxylamine, nitrosomenthene is re-formed, a proof

that the latter is a true oxime. The authors also discuss the bearings of recent work on the constitution of the menthol group.

L. T. T.

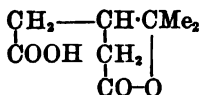
Oxidation of Cyclic Compounds. By G. WAGNER (*Ber.*, 27, 1636—1654).—Menthene, $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2\cdot\text{CH} \\ | \\ \text{CH}_2-\text{CH}_2\cdot\text{C}\cdot\text{CHMe}_2 \end{array}$ (1 mol.), was oxidised at about 0° with a 1 per cent. solution of potassium permanganate (containing 1 atom of oxygen); the products were a glycol, $\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2-\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CHMe}_2$; the corresponding keto-alcohol; a keto-acid (δ -isobutyryl- β -methyl-valeric),



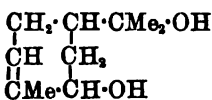
methyladipic acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, and acetic acid. The *keto-alcohol* boils at 104·5—105·5° under 13·5 mm. pressure, and has a sp. gr. = 0·9881 at 0°/0°; with phenylcarbimide it yields a *carbamate*, $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{10}\text{H}_{17}\text{O}_2$, melting at 155—157°, and with hydroxylamine an *oxime*, melting at 132—133°. The *glycol* is a viscid liquid, boiling at 129·5—131·5° under 13 mm. pressure; after a time it partially solidifies to crystals melting at 76·5—77°. Acetic anhydride at 150° converts it into a *diacetate*, boiling at 165—172° (mixed, perhaps, with some monacetate, or with the acetate of an unsaturated alcohol), but also dehydrates a portion, forming a *terpene* which boils at 179—180°, and is probably identical with the product obtained by Berkenheim (*Abstr.*, 1892, 867) from menthene dibromide and potash. The methyladipic acid melts at 93—94·5°; immediately after solidifying, at 84·5°; after a short interval, again at 93—94·5°. The *keto-acid* is a liquid boiling at 288—290° (under 19 mm. pressure, at 182—185°). (In an attempt to prepare menthene by the action of strong sulphuric acid on menthol, it was found that menthane, that is hexahydrocymene, is the chief product.)

Pinol is oxidised by potassium permanganate, as above, to the glycol, $\text{C}_{10}\text{H}_{16}\text{O}(\text{OH})_2$; this crystallises from ether and ethylic acetate in rhombic pyramids melting at 126—127°, from water in monoclinic tables melting at 128—129°, and with acetic anhydride yields a diacetate, which boils at 166—167° under 17 mm. pressure, and does not solidify. (Wallach obtained rather different data; possibly he was working with a stereoisomeric pinol.) If permanganate was used in quantity equivalent to 3 atoms of oxygen per mol. of pinol, there were formed, in addition to pinol glycol, terpenylic acid, and a trace of terebic acid. Terpenylic acid is thus the main product of the further oxidation of pinol, and from the known formula of this acid (Schryver, *Trans.*, 1893, 1338), the formula given below for pinol is deduced. Now pinol is formed by the action of dilute sulphuric acid on a compound which Sobrero obtained by the action of oxygen on turpentine in the presence of light; this compound is further identical with Wallach's pinol hydrate, obtained by adding hydrogen bromide to pinol, and then displacing the bromine by hydroxyl. Since this compound is formed from pinol, the formula below

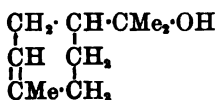
is assigned to it, in preference to Wallach's formula, and it is supposed that, when hydrogen bromide is added to pinol, the double bond of the latter is not attacked, but the bond $\text{O}-\text{CH}$ is destroyed. Pinol would thus be a dihydric alcohol, or glycol, and would still contain a double bond; this is in harmony with the fact that, when oxidised with permanganate, it does actually act like such a compound, yielding a *tetrahydric alcohol*, $\text{C}_{10}\text{H}_{20}\text{O}_4$, melting at $155.5-156^\circ$. The author also assigns new formulæ to several members of the terpene group; the most important of these are reproduced below, but the reasons which lead to their adoption it is impossible to give in an abstract.



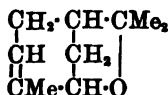
Terpenylic acid.



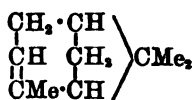
Pinol hydrate.



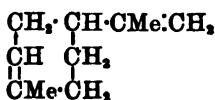
Terpineole.



Pinol.



Pinene.



Limonene.

C. F. B.

Oxidation of Menthone. By O. MANASSE and H. RUPE (*Ber.*, **27**, 1818—1822; compare Semmler, *Abstr.*, 1893, i, 396).— β -methyladipic acid is produced almost quantitatively by the oxidation of menthone with dilute potassium permanganate solution at ordinary temperatures; it can be purified by precipitation from benzene by means of light petroleum, and melts at $88.5-89^\circ$. The electrolytic conductivity, $k = 0.00397$; that of the synthetical acid, $k = 0.00401$, $\mu_\infty = 351$. The acid is dextrogyrate, $[\alpha]_D = +8.42$. The *copper salt*, when precipitated at the ordinary temperature, is pale green and amorphous, but when heated with water, it forms slender, bluish-green, concentric prisms. The *iron salt* is yellowish-red; no sparingly soluble salts of the alkaline earths, zinc, or lead were obtained. The *anhydride* is formed by the action of acetic chloride on the acid, but not by heating the acid above its melting point; it is a colourless oil from which the acid is regenerated by exposure to the air. This is the first anhydride of the adipic series of acids which has been prepared, and its formation shows the influence of alkyl radicles in causing the convergence of the carboxyl groups in dicarboxylic acids. The oxidation of menthone proceeds in a similar manner to that of menthol, the intermediate keto-acid,



being quickly, and almost completely, converted into β -methyladipic acid.

J. B. T.

Maclurin and Phloretin. By G. CIAMICIAN and P. SILBER (*Ber.*, **27**, 1627—1633).—Maclurin, $C_{13}H_{10}O_6$ (which is shown to crystallise with H_2O), when boiled with acetic anhydride and anhydrous sodium acetate, yields a compound, $C_{23}H_{18}O_{10}$, melting at $181-182^\circ$, and having the composition of a pentacetyl derivative, less 1 mol. of water. Now, if, as is sometimes supposed, maclurin is a phloroglucol salt of protocatechuic acid, it could only yield a tetracetyl derivative. Its actual behaviour, however, resembles that of cotoin (this vol., i, 256), and it is probably similarly constituted (being thus a ketonic compound), in spite of the fact that it does not react with phenylhydrazine or hydroxylamine. The compound, $C_{23}H_{18}O_{10}$, is hydrolysed by boiling with hydriodic acid, but the yellow product (? $C_{15}H_{10}O_6$), melting above 270° , was not obtained pure.

Phloretin, $C_{16}H_{14}O_6$, behaves in a similar manner, yielding a substance, $C_{23}H_{20}O_8$, which has the composition of a tetracetyl derivative, less 1 mol. of water. This substance melts at 173° , and yields, on hydrolysis, a yellowish compound, $C_{17}H_{14}O_6$, melting at 213° . These reactions again are probably analogous to those of cotoin.

C. F. B.

Jalapin. By T. POLECK (*Arch. Pharm.*, **232**, 315—320).—The author replies to the strictures of Spirgatis (*Arch. Pharm.*, **232**, 241) on his previous work on jalapin (*Abstr.*, 1893, i, 225).

W. J. P.

Reduction of α -Ethyl Pyridyl Ketone; Non-identity of α -Ethylpiperylalkine with Active Pseudoconhydrine. By C. ENGLER and F. W. BAUER (*Ber.*, **27**, 1775—1779; *Abstr.*, 1891, 1504).—The authors have further studied the coniine and intermediate compounds obtained by the reduction of α -Ethyl pyridyl ketone as already described.

Coniine boils at $166-168.5^\circ$. The *hydrochloride* crystallises in silvery needles, and melts at $208-210^\circ$. The *platinochloride* is obtained as an oil which soon crystallises in orange-red nodules. The *double salt* with cadmium iodide has the same properties as the salt obtained from natural coniine. Optically active coniine can be prepared from the inactive synthetical substance by Ladenburg's method, that is, by crystallisation of the tartrate.

The high-melting modification of α -ethylpiperylalkine (m. p. $99-100^\circ$) is not identical with pseudoconhydrine (m. p. $101-102^\circ$), as is proved by a comparison of their salts as given below. The hydrobromides and hydrochlorides of both bases are very similar, and crystallise in white, hygroscopic needles. The salts of pseudoconhydrine are, however, more stable on exposure to air. The platinochlorides are very similar, and do not crystallise. *Ethylpiperylalkine cadmium iodide* crystallises in lustrous crystals, and melts at $121-122^\circ$. *Pseudoconhydrine cadmium iodide* is an oil which cannot be obtained crystalline. The flocculent precipitates which phosphomolybdic acid and mercuric chloride give with both bases are very similar. The difference of the two bases is clearly shown in the properties of the aurochlorides.

α-Ethylpiperylalkine aurochloride crystallises in beautiful yellow prisms, and melts at 138—139°. The crystals belong to the monoclinic system (110) : (1 $\bar{1}$ 0) = 105° 27'; (110) : (001) = 87° 30'.

The aurochloride from pseudoconhydrine separates in beautiful yellow, rhombic crystals, and is identical with conhydrine aurochloride. The measurement of the crystals gave

$$a : b : c = 0.68059 : 1 : 0.73101; (110) : (1\bar{1}0) = 68^\circ 28' 42'', (011) : (0\bar{1}1) = 72^\circ 20'.$$

Thus, in the preparation of the aurochloride, pseudoconhydrine is converted into conhydrine.

The low-melting modification of *α-ethylpiperylalkine* has now been obtained in long, sharp-pointed needles melting at 69.5—71.5°. It is optically inactive. The *hydrochloride*, *hydrobromide*, and *platinochloride* are indistinguishable from the salts of the modification of high-melting point. The *aurochloride* crystallises in prisms, and melts at 135—136°. The *double salt* with *cadmium iodide* is a brownish-yellow oil which only crystallises with great difficulty.

E. C. R.

Ethereal Salts and Amides of Pyridinecarboxylic acids. By C. ENGLER and others (*Ber.*, 27, 1784—1789; compare H. Meyer, this vol., i, 425).—Methylic picolinate, obtained in the usual way, boils at 232° (uncorr.), and melts at 14°. The *platinochloride* crystallises in orange-yellow prisms with 2H₂O.

Ethylic picolinate is a colourless liquid, and boils at 243° (uncorr.). *Propylic picolinate* is a pale yellow oil, and boils at 258°; the *platinochloride* crystallises in orange-yellow plates. *Isobutylic picolinate* is a colourless oil, and boils at 261.5°. *Amylic picolinate* is a yellowish oil, boils at 278—279° with slight decomposition, and has an unpleasant odour; the *platinochloride* crystallises in beautiful yellow needles.

Picolinamide, C₆NH₄CONH₂, is most easily obtained by treating the ethylic salt with concentrated aqueous ammonia. It forms beautiful crystals, and melts at 107°. The *hydrochloride* crystallises in lustrous leaflets, which effloresce on exposure to air.

Picolinanilide, C₆NH₄CONHPh, melts at 76°. The *orthotoluidide* crystallises in silky needles, and melts at 64.5°; the *paratoluidide* in tablets melting at 104°; whilst the *naphthalide* crystallises in reddish needles, and melts at 128°.

The following compounds of nicotinic acid are described. The *methylic salt* boils at 204°, and melts at 38°. The *ethylic salt* boils at 218°. The *propylic salt* is a colourless oil, and boils at 232°. The *amylic salt* is a yellow oil, and boils at 259°. The *amide* crystallises in slender interlacing needles, and melts at 125°.

Quinolinic acid.—The *dimethylic salt* crystallises in beautiful lustrous leaflets, and melts at 53—54°. The *diethylic salt* is a yellowish oil, and boils and slightly decomposes at 280—285°. The *dipropylic salt* is a bright yellow oil, boils above 300°, has a penetrating odour, and darkens on exposure to air. The *diamide* melts at 209°.

Quinolinicimide, C₆NH₃(CO)₂NH, is obtained by heating the diamide at 200—209° as long as ammonia is evolved. It forms

colourless crystals, and melts at 227°. The *acetyl-compound* crystallises in slender, white needles, and melts at 161—162°. The *potassium salt* is obtained by allowing the imide and potassium hydroxide dissolved in alcohol to remain some time. It crystallises in aggregates of white needles, which contain $1\text{H}_2\text{O}$ after drying at 100°, and is very hygroscopic.

Phenyl quinolinicimide, $\text{C}_6\text{NH}_2(\text{CO})_2\text{NPh}$, is obtained by heating the imide with aniline in a reflux apparatus. It crystallises in lustrous, interlacing needles, and melts at 228°. The *platinochloride* crystallises in red needles.
E. C. R.

Preparation of Quinoline. By J. WALTER (*J. pr. Chem.*, [2], 49, 549—550).—For the performance of Skraup's method of preparing quinoline a flask of large capacity is necessary in order to provide for the froth generated during the reaction. This inconvenience can be avoided by heating the nitrobenzene in a flask provided with a reflux condenser and a dropping funnel, from which the mixture of aniline, glycerol, and sulphuric acid may be added by degrees. In such an arrangement a flask of 800 c.c. capacity will suffice for a charge of 48 grams of nitrobenzene, whereas, by the old method, a 2000 c.c. flask was necessary for 24 grams of nitrobenzene. The addition of the other constituents to 48 grams of nitrobenzene should be spread over three-quarters of an hour, and to keep their viscosity low the dropping funnel should be surrounded by a leaden steam coil. The distillation of the quinoline in steam may be effected in an iron vessel.
A. G. B.

3 : 4 : 4'-Tribromoquinoline and 2 : 3 : 4 : 4'-Tetrabromoquinoline. By A. CLAUS and K. REINHARD (*J. pr. Chem.*, [2], 49, 525—539; compare *Abstr.*, 1888, 163; 1893, i, 667; this vol., i, 52, 53, 54, 382).—3-Bromoquinoline *methiodide* crystallises in yellow needles, and melts and partially decomposes at 278°. The *methochloride* forms colourless tables, begins to decompose at 224°, and melts at 238°; its *platinochloride* is described. The *ethiodide* melts and decomposes at 194°. The *ethochloride* melts at 145°.

By nitration in sulphuric acid, 3-bromoquinoline yields 4 : 3-nitro-bromoquinoline (*Abstr.*, 1890, 267), the *methochloride* of which crystallises in vitreous, topaz-coloured, rhombic prisms, and melts at 203°. The *platinochloride* of the methochloride is described. 4 : 3-Dibromoquinoline melts at 135°.

1 : 3-Nitrobromoquinoline is formed when 3-bromoquinoline is digested with nitric acid (sp. gr. 1.52) for several days. It crystallises in small, colourless, vitreous needles, melts at 170°, and is less soluble in hot alcohol than is the 4 : 3-derivative. The *platinochloride* is anhydrous, and melts at 265—268°. 1 : 3-Amidobromoquinoline crystallises in lustrous needles, which are generally tinted, melts at 76—77°, and is slightly soluble in hot water; the *hydrochloride* forms yellow-red needles with $2\text{H}_2\text{O}$, and melts at 236—237°; the *platinochloride* is described.

Both 3 : 1- (*loc. cit.*) and 3 : 4-bromoquinolinesulphonic acids are obtained by sulphonating 3-bromoquinoline with anhydro-sulphuric

acid, the proportion between them depending on temperature and concentration; the acids may be separated by means of their potassium salts, that of the 3 : 1-acid being the less soluble. The potassium, calcium ($\text{1H}_2\text{O}$), and barium salts of 3 : 1-bromoquinoline-sulphonic acid are described.

3 : 4-Bromoquinolinesulphonic acid crystallises with $\text{1H}_2\text{O}$ in tables, dissolves freely in hot water, and does not melt at 330° . The potassium ($\text{1}\frac{1}{2}\text{H}_2\text{O}$), calcium ($5\text{H}_2\text{O}$), ammonium, and barium salts are described.

The product of the bromination of 3 : 1-bromoquinolinesulphonic acid, described by Claus and Zuschlag (*loc. cit.*) as a tribromoquinoline melting at 185° , is a mixture of 1 : 3 : 4'-tribromoquinoline (m. p. 169°) and 1 : 3 : 4 : 4'-tetrabromoquinoline (m. p. 205°) (compare Abstr., 1891, 82). The bromination of 3 : 4-bromoquinoline-sulphonic acid yields 3 : 4 : 4'-tribromoquinoline (m. p. 149°) and 1 : 3 : 4 : 4'-tetrabromoquinoline.

A. G. B.

Constitution of Cycloïd Systems. By W. MARCKWALD (*Annalen*, 279, 1—23).—The author replies to Claus (this vol., i, 174). He considers that the results of his previous investigation (Abstr., 1893, i, 603) may be thus summarised:—The existence of para-bonds in benzene has never been recognised in a single instance, but, on the contrary, benzene-derivatives exhibit a resistance to the formation of para-bonds. Kekulé's benzene formula, granting that in poly-cycloïd systems oscillation is suppressed, does not stand in conflict with any known facts.

The fresh evidence brought forward by Bamberger and Hoffmann (this vol., i, 139) in support of the centric formulæ as an explanation of the hydrogenation phenomena in anthracene derivatives is criticised. The phenomena there cited depend, according to the author, upon the peculiar constitution of the central benzene nucleus. The constitution of other cycloïd systems is also discussed from the point of view of centric formulæ.

The deductions which Stohmann draws from his calorimetric determinations (*Sächs. Ges. Wissensch.*, 1893, 477; also this vol., ii, 80) as to the constitution of benzene (compare also, Brühl, this vol., i, 366), are regarded by the author as premature. The author also refers to Schöpf's work on phenonaphthacridine (this vol., i, 41), which, he contends, furnishes no evidence against his views.

The following experiments are brought forward by the author as a fresh support of Körner's quinoline formula:— α -Amidelepidine (Ephraim, Abstr., 1892, 1488) boils at 320° undecomposed. When treated according to the Skraup or Doebner-Miller methods, the greater portion remains unaltered.

γ -Amidoquinaldine (Ephraim, Abstr., 1893, i, 727) melts at 162 — 163° ; and boils at 333° ; the *platinochloride* melts at 223° with decomposition; and the *picrate* melts at 197 — 199° .

α -Methyl- γ -quinoquinoline, $\text{C}_{13}\text{N}_2\text{H}_{10}\text{N} \leq \begin{array}{c} \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N}=\text{CH} \\ \text{CMe}\cdot\text{C}\cdot\text{CH}\cdot\text{CH} \end{array}$, is obtained

from γ -amidoquinaldine or its salts by Skraup's method; it forms small, yellowish crystals, melts at 206° , and boils undecomposed

above 360°. The *platinochloride* becomes brown at 250° without melting, and the *picrate* melts at 243°.

aa-Dimethyl-γ-quinoline, $N \begin{smallmatrix} C_6H_4 \cdot C \cdot N = CMe \\ \diagup \\ CMe \cdot C \cdot CH : CH \end{smallmatrix}$, is prepared from *γ-amidoquinaldine* by the Doebner-Miller method; it crystallises in long, felted needles, melts at 104°, and boils undecomposed above 360°; the *platinochloride* decomposes without melting above 200°; and the *picrate* sinters together and decomposes at 225°.

A. R. L.

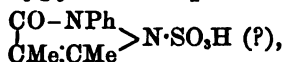
Condensation Products of Aromatic Hydrazides of Ethylic Acetoacetate. Indole and Pyrazole Derivatives. By C. WALKER (*Amer. Chem. J.*, 16, 430—442).—In preparing these hydrazides there is a great tendency towards the separation of alcohol and formation of pyrazolones; this, however, is in great measure prevented if the ethereal salt is added to the hydrazine dissolved in a little absolute ether, instead of the hydrazine being, as is usual, added to the salt.

Ethylic paratolyl-α-methylindole-β-carboxylate,



is formed by the action of strong sulphuric acid on ethylic acetoacetate paratolylhydrazide. It crystallises in regular octahedra and tetrahedra, melts at 163—163·5°, and is readily soluble in alcohol, ether, benzene, and acetone. It gives the indole splinter reaction, and when heated with potash at 150° yields the dimethylindole described by Raschen (*Abstr.*, 1887, 956). *Ethylic acetoacetate orthotolylhydrazide* is crystalline, melts at 95—97°, and is soluble in the usual organic solvents. *Ethylic orthotolyl-α-methylindole-β-carboxylate* forms monoclinic prisms melting at 173° and soluble in alcohol and ether. Whilst hydrazides of substituted ethylic acetoacetates yield with sulphuric acid a certain amount of the indole derivatives, the main products of the reaction are pyrazolonesulphonic acids, more of the latter being formed the higher the temperature of the reacting compounds.

Ethylic α-indolepropionate, $C_6H_4 \begin{smallmatrix} CH \\ \diagup \\ NH \end{smallmatrix} > CHMe \cdot COOEt$, from ethylic methylacetoacetate phenylhydrazide, forms white crystals melting at 136°, is soluble in organic solvents, and gives the indole splinter reaction. *Phenyldimethylpyrazolone-sulphonic acid*,



crystallises from boiling water in white needles, is sparingly soluble in all solvents, and is still solid at 300°. It gives Knorr's pyrazoline reaction. With ethylic ethylacetoacetate phenylhydrazide, the sulphuric acid indole reaction seems to proceed differently, ethylamine being separated, and the same ethylic α-methylindole-β-carboxylate produced as is formed by the action of sulphuric acid on ethylic acetoacetate phenylhydrazide (*Abstr.*, 1893, i, 368). *1-Phenyl-3-methyl-4-benzyl-5-pyrazolonesulphonic acid*, formed by the action of strong

sulphuric acid on the phenylhydrazide of ethylic benzylacetoacetate, crystallises in white flakes, easily soluble in hot benzene or chloroform, more sparingly in alcohol. It is still solid at 300°, forms stable salts which are non-crystallisable, and gives Knorr's pyrazoline reaction. Attempts to eliminate the sulphonic group so as to form phenylmethylbenzylpyrazolone were unsuccessful, although the above sulphonic acid was reproduced by sulphonating the latter pyrazolone. 1-Orthotolyl-3-methyl-5-pyrazolone, obtained by the spontaneous decomposition of ethylic acetoacetate orthotolylhydrazide at ordinary temperatures, forms quadratic prisms or needles melting at 143—144°. 1-Phenyl-3-methyl-4-benzyl-5-pyrazolone forms glistening scales melting at 136°. It is readily soluble in alkali, sparingly in boiling water.

Phenylmethylethoxypyrazole (*loc. cit.*) is best obtained by the action of acetic chloride on an ethereal solution of the hydrazide at very low temperatures (−15°). It crystallises in hexagonal prisms or needles, melts at 68—68.5°, is insoluble in water but soluble in organic solvents. It gives Knorr's pyrazoline reaction, but does not give a coloration with ferric chloride. When heated with alcoholic potash, it yields phenylmethylhydroxypyrazole, which is readily soluble in alkalis and in organic solvents, crystallises in orange needles, and melts at 196—198°. It gives no coloration with ferric chloride, but Knorr's reaction gives a permanent green coloration. Its salts are tolerably stable, and are mostly soluble in water. L. T. T.

Isopyrazolones. By S. RUHEMANN (*Ber.*, 27, 1658—1663).—When ethylic dicarboxylate, $\text{CH}(\text{COOEt})_2$, is mixed with excess of hydrazine hydrate, there are formed ethylic isopyrazolonecarboxylate, its hydrazine salt, malonylhydrazide, and ethylic malonate; the split thus takes place between the two CH groups. Ethylic methylidicarboxylate reacts in a similar manner. Malonylhydrazide, $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$, melts at 154°. Ethylic isopyrazolonecarboxylate, $\begin{array}{c} \text{NH}\cdot\text{CH} \\ | \\ \text{NH}\cdot\text{CO} \end{array} > \text{C}\cdot\text{COOEt}$, melts at 180—181°; its hydrazine salt, $\text{C}_6\text{H}_5\text{N}_2\text{O}_3\cdot\text{N}_2\text{H}_4$, softens at 140°. It forms a diargentate salt which, when boiled with methyl iodide, yields ethylic dimethylisopyrazolonecarboxylate, $\begin{array}{c} \text{NMe}\cdot\text{CH} \\ | \\ \text{NMe}\cdot\text{CO} \end{array} > \text{C}\cdot\text{COOEt}$, melting at 88—89°. It is further hydrolysed by boiling with aqueous potash, and, on acidifying the solution, white isopyrazolonecarboxylic acid is precipitated. This, however, is unstable, and is converted by boiling water into isopyrazolone, $\begin{array}{c} \text{NH}\cdot\text{CH} \\ | \\ \text{NH}\cdot\text{CO} \end{array} > \text{CH}$, which melts at 165°. It will be noticed that displacement of the H in the NH groups in isopyrazolone and its derivatives produces a lowering of the melting point. C. F. B.

Conversion of Thiocumazone into Thioquinazolines. By C. PAAL and O. COMMERELL (*Ber.*, 27, 1866—1870).—Thiocumazone (*Abstr.*, 1893, i, 25) reacts with primary aromatic bases to form thioquinazolines, identical with those described by Busch (*Abstr.*, 1892,

1495; this vol., i, 146). Aniline, for example, produces 3-(*n*)-phenyl-tetrahydro-2-thioquinazoline, melting at 260°. This reaction serves as an additional proof of the formula already adopted for thiocumazone.

When reduced in alcoholic solution with metallic sodium, thiocumazone is quantitatively converted into orthotoluidine.

A. H.

Dithiourazole and its Derivatives. By M. FREUND (*Ber.*, 27, 1774—1775; see also this vol., i, 97).—Thiocarbamides of the type $R \cdot NH \cdot CS \cdot NH \cdot NH \cdot CS \cdot NH \cdot R$ decompose in two ways, yielding compounds $C_2H_5RN_2S_2$ or $C_2H_5R_2N_4S$.

The following compounds of the first type have been prepared:—*dithiourazole*, $C_2H_5N_2S_2$, m. p. 245°; *methyl dithiourazole*, $C_2H_5MeN_2S_2$, m. p. 187°; *ethyl dithiourazole*, m. p. 140°; *allyl dithiourazole*, m. p. 130°; and *phenyl dithiourazole*, m. p. 215°. These compounds are strong acids, yield crystalline salts, contain two nitroso-groups, and may be converted quantitatively into the corresponding azo-compounds.

The compounds of the second type have basic properties; the following have been prepared:—*Imidothiourazole*, $C_2H_5N_4S$, m. p. 210—212°; *methyl imidoethylthiourazole*, $C_2H_5Me_2N_4S$, m. p. 177°; and *ethyl imidoethylthiourazole*, m. p. 173°.

E. C. R.

Iodides of Narceïne. By G. B. FRANKFORTER (*J. Amer. Chem. Soc.*, 16, 361—363).—The author has re-examined the iodides of narceïne. The *blue iodide* formed by treating crystals of narceïne directly with iodine has the formula $(C_{23}H_{27}NO_3)_2I_2 + 3H_2O$, forms prismatic needles slightly soluble in water, loses its water of crystallisation at 100°, and melts at 176—177°, or if rapidly heated at 180—181°. When narceïne is treated with alcoholic solution of iodine, a greyish-blue substance is formed, which, on exposure to air, or when gently heated, changes to a *red iodide* of the formula $(C_{23}H_{27}NO_3)_2I + 3H_2O$. At 100° it loses its water, forming a brick-red powder melting at 181°, and insoluble in water, alcohol, and ether. Both iodides, if just neutralised with soda, yield white, hexagonal prisms which are now under investigation.

L. T. T.

Merochinine and Cincholeupone. By W. KOENIGS (*Ber.*, 27, 1501—1507; compare this vol., i, 392).—Merochinine, $C_8H_{11}NO_2$, is formed by the oxidation of cinchonine with potassium dichromate and sulphuric acid. When it is heated with dilute hydrochloric acid at 240°, a base of the formula $C_8H_{11}N$ is formed, the yield being considerably increased if an oxidising agent, such as mercuric chloride, be also present. This base appears to be identical with the β -collidine obtained by Oechsner de Coninck (*Ann. Chim. Phys.*, [5], 27, 469). On oxidation, it yields two acids which are most probably cinchomeronic acid, $C_8H_7N(COOH)_2$, and homonicotinic acid, $C_8H_7MeN \cdot COOH$. The base derived from merochinine is, therefore, γ -methyl- β -ethylpyridine. Merochinine, like cincholeupone hydrochloride, when distilled with zinc dust, yields a small amount of β -ethylpyridine.

The mother liquor of apocinchine contains *dihydrocinchine*,

$C_{15}H_{21}N_3$, which may be crystallised from alcohol, and melts at 145° . Its *platinochloride* does not melt below 265° , whilst its *picrate* melts at 197° . Towards hydrobromic acid this base behaves in a different manner from cinchine itself, no elimination of ammonia occurring. Aqueous phosphoric acid at 170 – 180° , on the other hand, decomposes both bases in a similar way, lepidine being formed, accompanied by merochinine in the case of cinchine, and by cincholeupone in that of dihydrocinchine. The dihydrocinchine was probably derived from dihydrocinchonine contained in the original commercial cinchonine, and it is, therefore, probable that the cincholeupone, which is obtained by the oxidation of commercial cinchonine, is formed at the expense of the dihydrocinchonine present, and is not a direct oxidation product of pure cinchonine.

Dihydrocinchine is also decomposed by phosphoric acid, but the product which accompanies the lepidine has not yet been examined. The results so far obtained seem to show that merochinine contains an imido- and a carboxyl-group, and is derived from γ -methyl- β -ethylpyridine, and this throws some light on the structure of quinine and cinchonine.

A. H.

Conhydrine and Pseudoconhydrine. By C. ENGLER and A. KRONSTEIN (*Ber.*, 27, 1779–1784).—When pure pseudoconhydrine (m. p. 101 – 102°) is dissolved in an excess of boiling light petroleum, and ether added to the solution, a modification separates in large, transparent leaflets. The authors name this modification *b*-pseudoconhydrine, and the other modification (m. p. 101 – 102°) *a*-pseudoconhydrine.

b-Pseudoconhydrine melts at 52 – 69° . The crystals always contain minute drops of the solvent; but as the melting point is always the same, whatever solvent is employed, there is no doubt that a true modification is present. This modification is converted into *a*-pseudoconhydrine, on leaving it for some time over calcium chloride, on heating at 200° , on sublimation, or on crystallisation from a small quantity of light petroleum, ether, or chloroform. A microcrystallographic examination of the conversion of *b*-pseudoconhydrine into *a*-pseudoconhydrine shows that by cautiously warming the *b*-modification it is converted into an enantiotropic modification (*c*-pseudoconhydrine), which on cooling is reconverted into the *b*-form.

When *a*-pseudoconhydrine is boiled for some hours with light petroleum in a reflux apparatus, it is partially converted into conhydrine and *b*-pseudoconhydrine. The latter, when treated in a similar way, is partially converted into conhydrine and *a*-pseudoconhydrine.

The authors were unable to convert conhydrine into an isomeric modification by heating it with solvents. A negative result was also obtained with α -ethylpiperyllalkaline.

E. C. R.

Preparation of Cocaine from the Allied Alkaloids. By A. EINHORN and R. WILSTÄTTER (*Ber.*, 27, 1523–1524).—This has hitherto been carried out by treating the alkaloids with concentrated hydrochloric acid, so as to obtain ecgonine, and then preparing

cocaine from this by converting it into the benzoyl-derivative, followed by etherification. A simpler plan is to heat the alkaloïds with methylic alcohol and sulphuric acid, or in a current of hydrogen chloride; in this case the methylic ether of ecgonine is directly obtained, and merely requires to be converted into the benzoyl compound. If ethylic alcohol is employed, the ethylic ether of ecgonine is obtained.

A. H.

Canadine: A Third Alkaloid from the Root of Hydrastis Canadensis. By E. SCHMIDT (*Arch. Pharm.*, 232, 136—154).—The existence of a third alkaloid in *Hydrastis canadensis* has not been hitherto clearly proved. The author, by taking advantage of the slight solubility in cold water of its nitrate, has isolated a new alkaloid from this source, in addition to berberine and hydrastine.

Canadine, $C_{20}H_{21}NO_4$, was obtained in colourless needles, which become yellow on exposure to light, and melt at 132.5° . With the exception of the sulphate, its salts with inorganic acids are characterised by their sparing solubility. An alcoholic solution of canadine is neutral to litmus, and is strongly lævogyrate, this property also belonging to aqueous solutions of its salts. The alkaloid dissolves in nitric acid with production of a yellow colour, whilst with vanadic anhydride and sulphuric acid it gives an olive-green, changing to brownish-black. Erdmann's reagent and Fröhde's reagent develop a transient olive-green coloration, which rapidly becomes brownish-red; a bluish-green colour, due to the formation of Prussian blue, is produced when the solution of a canadine salt is added to a mixture of potassium ferricyanide and ferric chloride.

The *sulphate*, $C_{20}H_{21}NO_4 \cdot H_2SO_4$, crystallises in large, colourless plates, associated with varying quantities of yellow needles, consisting of $C_{20}H_{21}NO_4 \cdot H_2SO_4 + H_2O$. The *hydrochloride* and *nitrate* are colourless salts which are only sparingly soluble in cold water. The *platinochloride*, *aurochloride*, and *methiodide* have been prepared and analysed, the latter forming pale yellow crystals melting at $228-232^\circ$; moist silver oxide converts the methiodide into an alkaline compound, which yields a *platinochloride* of the formula $(C_{20}H_{20}HNO_4)_2 \cdot Me_2PtCl_6$.

Canadine, when heated in alcoholic solution with iodine, is converted into berberine hydriodide. This reaction, coupled with the fact that berberine sulphate is present in solutions of canadine sulphate which have been exposed to light and air, suggests the probability of canadine being a tetrahydroberberine, isomeric with hydroberberine, the isomerism between these compounds depending on the different positions in the berberine molecule which it is possible for hydrogen atoms to assume.

M. O. F.

Oxidation of Proteïds by Potassium Permanganate. By S. BONDZYŃSKI and L. ZOJA (*Zeit. physiol. Chem.*, 19, 225—238).—Maly described, as the product of oxidation of egg-white by potassium permanganate, a substance, oxyprotoesulphonic acid (Abstr., 1885, 824), in which the amounts of carbon and nitrogen are approximately in the same proportion as in albumin. In the present research, this substance was prepared from pure proteïds—crystals of egg-albumin and

of oxyhæmoglobin. In the case of casein, which differs from albumin in containing phosphorus in its molecule, the results of analysing fractions of the oxidation product show it to consist of two substances.

W. D. H.

Crystallised and Ash-free Albumin. By E. HARNACK (*Zeit. physiol. Chem.*, 19 299—300).—Polemical. The author states that he has never cast aspersions or doubts on Hofmeister's work on crystalline egg-albumin, as Bondzyński and Zoja consider. He only adheres to his previous statement, that his ash-free albumin forms a crystalline compound with ammonium sulphate which is poor in proteid and rich in ammonia.

W. D. H.

Proteids of Egg-White. By R. T. HEWLETT (*Proc. physiol. Soc.*, 1894, 9—12).—The so-called globulin of white of egg gives most of the reactions of nucleo-albumin, but phosphorus determinations have yet to be made to confirm the supposition.

With regard to the albumin, not only does fractional heat coagulation suggest the presence of two or more proteids, but fractional precipitation by ammonium sulphate tends in the same direction; moreover, some of the fractions are precipitated by both normal and tribasic lead acetate, others only by the latter.

Ramsden found that prolonged heating for days brings down albumins at temperatures considerably below their usual coagulation point. If thymol had been used as an antiseptic in these experiments, a source of error was introduced, as this substance and, to a less degree, camphor precipitate proteids slowly.

W. D. H.

Albumone. By R. BRUNNER (*Inaug. Diss. Bern.*, 1894).—Chabrié (*Abstr.*, 1892, 224) prepared from human blood serum a new proteid he called albumone. Ox blood, by similar treatment, yields the same substance. It does not, however, pre-exist in the serum, and the present research shows that it is formed during the process of heat coagulation, partly from serum-albumin, partly from serum-globulin.

W. D. H.

Specific Rotatory Power of Fibrinogen. By F. MITTELBACH (*Zeit. physiol. Chem.*, 19, 289—298).—Hammarsten states that on heating a solution of fibrinogen to 56°, a globulin is split off from it which coagulates at 65°. The present research does not confirm this, and Hammarsten's result is explained in the same way that Haycraft explains the result of fractional heat coagulation generally. Great dilution raises the temperature of heat coagulation of fibrinogen to 65°, and dilution would occur if the greater part of the proteid were coagulated at 56° and removed by filtration. The specific rotatory power is given as $(\alpha)_D = -52.5^\circ$. Hermann (*Abstr.*, 1887, 1131) gives -43° .

W. D. H.

Organic Chemistry.

Relationships between Boiling Points, and between Melting Points. By G. COHN (*J. pr. Chem.*, [2], 50, 38—57).—The author calls attention to relationships which exist between the boiling points of (1) orthodiketones; (2) ketones and the acids from which they are derived in the manner indicated by the equation $\text{RCOOH} + \text{R'COOH} = \text{RCOR}' + \text{H}_2\text{CO}_3$; (3) aldehydes and the acids formed by their oxidation; (4) ethers and the alkyl haloïds and hydroxides from which they are derived in accordance with the equation $\text{RCI} + \text{R'OH} = \text{HCl} + \text{RR'O}$; (5) amines and aldehydes, an examination of which shows that the amines have approximately the same boiling points as have the aldehydes containing the same number of carbon atoms; (6) saturated and unsaturated compounds containing the same number of carbon atoms; these show approximately the same boiling points; (7) aromatic compounds containing COOH on the one hand, and those containing C_6H_5 in place of this COOH on the other hand; these have approximately the same boiling points; (8) methyl ketones, methylic salts, and chloranhydrides; these have approximately the same boiling points. Relationships between melting points are less marked; the author calls attention to several cases of these in conclusion (compare Schröder, *Abstr.*, 1883, 990; Baeyer, *Abstr.*, 1878, 3; Kipping, *Trans.*, 1893, 465). A. G. B.

Action of Heat on Ethylene. By V. B. LEWES (*Proc. Roy. Soc.*, 55, 90—107).—The action of heat on ethylene was studied at temperatures ranging from 600° to 1500° , the gas being passed through a platinum tube of 2 mm. bore heated through a length of 140 mm. Incidentally, the behaviour, under similar circumstances, of ethane, acetylene and methane, and of benzene vapour was investigated. The author concludes that, taking into consideration the complexity of the changes involved and the difficulty in obtaining great accuracy in gas analysis, these results seem to prove that the primary action of heat on ethylene may be represented by the equation $3\text{C}_2\text{H}_4 = 2\text{C}_2\text{H}_2 + 2\text{CH}_4$, whilst the final decomposition is that represented by previous observers, namely, $\text{C}_2\text{H}_4 = \text{C}_2 + 2\text{H}_2$; between these two extremes there occur a large number of interactions due to the polymerisation of the acetylene formed from the ethylene, and also at higher temperatures from the methane in accordance with the equation $2\text{CH}_4 = \text{C}_2\text{H}_2 + 3\text{H}_2$. C. F. B.

Preparation of Tetrachlorethylene and its Oxidation by Ozone. By A. BESSON (*Compt. rend.*, 118, 1347—1350).—The action of metals on carbon tetrachloride is either too slow and yields only C_2Cl_4 , or, at higher temperatures, becomes explosive, with liberation of carbon. Aluminium foil acts slowly, and the filings act very rapidly, especially in presence of iodine, but no useful quantity of

tetrachlorethylene is formed. The action of ordinary phosphorus becomes explosive at 200° , and that of red phosphorus is very slow even at 300° .

When hydrogen mixed with vapour of carbon tetrachloride is passed through a tube containing pumice heated to redness, decomposition takes place with incandescence and separation of carbon. At a temperature below redness the action is less violent, and the chlorides, CHCl_3 , CH_2Cl_2 , C_2Cl_6 , and C_3Cl_8 are obtained. With very porous pumice, and a temperature just below that at which separation of carbon begins, the yield of tetrachlorethylene may amount to as much as 10 per cent. of the original carbon tetrachloride.

Ozone acts very slowly on tetrachlorethylene at 0° , but at 30° oxidation takes place, and a small quantity of carbon oxychloride is given off. The chief product of oxidation is trichloroacetic chloride, $\text{CCl}_3\cdot\text{COCl}$, which, with water, yields hydrochloric and trichloroacetic acids. From this result it would seem that tetrachlorethylene should be represented by the formula $\text{CCl}_3\cdot\text{CCl}$. Careful fractionation, however, gives no evidence of the existence of two isomeric tetrachlorethylenes. It is noteworthy that Prud'homme has previously obtained trichloroacetic chloride by the oxidation of tetrachlorethylene by sulphuric anhydride at a temperature above 100° .

Tetrachlorethylene oxide, $(\text{CCl}_2)_2\text{O}$, seems, however, to be formed by the action of ozone, especially if the temperature does not exceed 10° . It boils at about 110° under a pressure of 20 mm., is insoluble in, and is not attacked by, water, and has a disagreeable odour. When exposed to air, it explodes at its boiling point. The quantity obtained was not sufficient for a complete analysis, but the proportion of carbon corresponds with the formula given.

C. H. B.

Action of Bromine on Diallyl. By K. KRASUSKY (*J. Russ. Chem. Soc.*, 25, 619—626).—If, in Berthelot and De Luca's method of preparing diallyl from allylic iodide and sodium, a copper flask is substituted for a glass one, the yield obtained rises to 87 per cent. of the theoretical.

Bromine was added drop by drop at 0° to an ethereal or chloroform solution of diallyl prepared in this way until it was permanently coloured. After the mixture had been left for 10 hours in the dark, the solvent was evaporated and the solid part of the residue separated from the comparatively small liquid part, which did not solidify in a freezing mixture. The liquid portion was dissolved in alcohol and fractionally precipitated by the addition of successive small quantities of water. The first portions precipitated, solidified on standing. The fractions which remained liquid were separated, dried, and distilled under 19 mm. pressure, fractions being collected at various temperatures between 100° and 180° , and the quantity of bromine in them determined. The bromine in the solid portions corresponded with the formula of the tetrabromide, $\text{C}_6\text{H}_{10}\text{Br}_4$; but the liquid portions always contained much less bromine than the tetrabromide, so that the conclusion of Ciamician and Anderlini, that the liquid is a stereoisomeride of the solid tetrabromide, is incorrect.

J. W.

Chlorination of Alcohol. By P. FRITSCH (*Annalen*, 279, 288—300).—According to Lieben (*Annalen*, 104, 114; *Ber.*, 3, 907), the action of chlorine on alcohol is, first of all, to produce aldehyde, which then reacts with 2 mols. of alcohol to form acetal; the further action of chlorine on this substance yields trichloroacetal, which is then decomposed into chloral alcoholate and ethylic chloride by the hydrogen chloride formed. The author's experiments show that when chlorine is passed into alcohol, the first product which can be isolated is monochloroacetal. As the chlorination proceeds beyond this point, increasing amounts of dichloroacetal are produced, and these two compounds are partially converted, by the hydrogen chloride formed, into di- and tri-chloroether respectively. This is shown by the fact that if a litre of alcohol be treated with 500 grams of chlorine, the hydrogen chloride removed by digestion with marble, and water added, only 100 grams of the mixed chloroacetals are obtained, whilst if half a volume of alcohol be added before the treatment with marble, 210 grams of the chloroacetals are obtained, the difference being the amount formed by the interaction of the alcohol with the chlorinated ether present.

If the temperature is maintained at 25—30°, and the chlorination continued, a heavy oil separates, and, finally, the chlorine ceases to be absorbed. This heavy layer (sp. gr. 1.32) consists chiefly of trichloroether, $\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt}$, along with smaller quantities of dichloroether and the hydrates of mono- and di-chloraldehyde. When this oil is distilled, the di- and tri-chloroethers are partially converted by the water present into the alcoholates of the corresponding chlorinated aldehydes, which then decompose on distillation, with evolution of hydrogen chloride, into water, chlorinated aldehydes, and chlorinated acetals.

The lighter layer of liquid (sp. gr. 1.2) is a concentrated solution of hydrogen chloride containing a small amount of dichloraldehyde.

If the temperature be now raised to about 42—45° and the chlorination again continued, a homogeneous liquid is obtained, the trichloroether being converted by the aqueous solution into dichloraldehyde alcoholate, which is then finally converted by chlorination into chloral alcoholate, the mono- and di-chloraldehyde being at the same time converted into chloral.

The course of the whole reaction may therefore be expressed by the following equations.

- (1.) $3\text{C}_2\text{H}_5\text{O} + 2\text{Cl}_2 = \text{CH}_2\text{Cl} \cdot \text{CH}(\text{OEt})_2 + 3\text{HCl} + \text{H}_2\text{O}.$
- (2.) $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OEt})_2 + \text{Cl}_2 = \text{CHCl}_2 \cdot \text{CH}(\text{OEt})_2 + \text{HCl}.$
 $\text{CHCl}_2 \cdot \text{CH}(\text{OEt})_2 + \text{HCl} = \text{CHCl}_2 \cdot \text{CHCl}(\text{OEt}) + \text{EtOH}.$
- (3.) $\text{CHCl}_2 \cdot \text{CHCl}(\text{OEt}) + \text{H}_2\text{O} = \text{CHCl}_2 \cdot \text{CH}(\text{OEt}) \cdot \text{OH} + \text{HCl}.$
 $\text{CHCl}_2 \cdot \text{CH}(\text{OEt}) \cdot \text{OH} + \text{Cl}_2 = \text{CCl}_3 \cdot \text{CH}(\text{OEt}) \cdot \text{OH} + \text{HCl}.$

The liquid obtained by Liebig (*Annalen*, 1, 221) by passing chlorine into cold alcohol, adding water, and thoroughly washing the oil with water, which was termed by him "heavy hydrochloric ether," is, in reality, a mixture of trichloroether with mono- and di-chloroacetal.

In order to prepare monochloroacetal, about 400—450 grams of chlorine is passed into a litre of alcohol of 94—99 per cent. at 25°

(until the specific gravity of the liquid is 1.02—1.03), $\frac{1}{2}$ litre of alcohol is added, the whole heated to 50—60°, digested with marble, precipitated with water, and fractionated. The yield amounts to about 200 grams. Dichloroacetal may also be readily prepared by passing chlorine into a litre of alcohol at a temperature of 25—30° as long as it is easily absorbed; a litre of alcohol is then added to the heavy layer which has been formed, the whole digested with marble, and the oil which is precipitated on adding water fractionated; about 850—900 grams are obtained.

A. H.

Mechanism of the Action of Chlorine on Isobutylic Alcohol.

By A. BROCHET (*Compt. rend.*, 118, 1280—1282).—Chlorine is rapidly absorbed by isobutylic alcohol at the ordinary temperature, and the liquid must be cooled. The chief product is unsymmetrical *dichloroisobutylic oxide*, $\text{CMe}_2\text{Cl}\cdot\text{CHCl}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CHMe}_2$, a refractive, very mobile liquid which boils at 192.5° under a pressure of 760 mm., and at 83° under a pressure of 15 mm.; $d_{15}^{15}/4^\circ = 1.031$; refractive index, $n_D = 1.437$. It has a pleasant ethereal odour when freshly distilled, but, when exposed to moist air, decomposes slightly, with evolution of hydrogen chloride. It seems probable that the action of chlorine on isobutylic alcohol first produces α -chloroisobutaldehyde, and the latter condenses with the unaltered alcohol in presence of the hydrochloric acid that is formed simultaneously.

Water has little action on dichloroisobutylic oxide at the ordinary temperature, but at 100° decomposes it rapidly with evolution of hydrogen chloride and formation of α -chlorisobutaldehyde and diisobutylmonochlorisobutyral, $\text{CMe}_2\text{Cl}\cdot\text{CH}(\text{OC}_2\text{H}_5)_2$. Alkali hydroxides and calcium and barium hydroxides induce a similar decomposition. Isobutylic alcohol, at its boiling point, and sodium ethoxide or sodium isobutyloxyde, at the ordinary temperature, also give rise to the same products. Diisobutylmonochlorisobutyral has an agreeable odour and boils at 218°; $d_{15}^{15}/4^\circ = 0.9355$; refractive index, $n_D = 1.426$. When heated with acetic anhydride in a sealed tube, it yields α -chlorisobutaldehyde and isobutylic acetate. When mixed with ethylic carbamate and saturated with hydrogen chloride, it yields chlorisobutylieneurethane identical with that obtained by the direct action of the aldehyde.

C. H. B.

Preparation of Methylic Nitrate. By G. BERTONI (*Chem. Centr.*, 1894, i, 623—624; from *Boll. chim. farmac.*, 33, 33).—Methylic nitrate may be safely prepared as follows: 160 grams of dried and finely-powdered ammonium nitrate is introduced into a tubulated retort, and a mixture of 100 grams of methylic alcohol with 100 grams of sulphuric acid allowed to flow in. The retort is then at once placed in a water bath at 100° (without a flame), when the colourless nitrate distils over, and should be washed with water and dried over calcium chloride.

L. T. T.

Ethylphosphoric acid. By J. CAVALIER (*Compt. rend.*, 118, 1275—1277).—The heat of neutralisation of ethylphosphoric acid, H_2EtPO_4 , by successive equivalents of different alkalis, is as follows.

	Sodium hydroxide.	Potassium hydroxide.	Ammonia.	Barium hydroxide.
1st Equivalent. .	15.59	15.73	14.44	16.30
2nd " ..	13.80	13.61	12.03	13.88
3rd " ..	0.86	0.85	0.53	0.18

It is obvious that ethylphosphoric acid behaves as if it had two distinct acid functions analogous to those of the oxy-acids of phosphorus, although the difference in thermal value between the first and second functions is less strongly marked.

With one equivalent of alkali, the solutions are neutral to methyl-orange; with two equivalents they are neutral to phenolphthalein; methyl-orange, therefore, serves as a useful indicator for the preparation of the acid salts of the general formula MHEtPO_4 . The sodium compound forms a crystalline deliquescent mass; the potassium salt is also crystalline and very deliquescent; the ammonium salt forms transparent crystals which alter but little when exposed to air. The barium salt crystallises with $1\text{H}_2\text{O}$ in nacreous plates which are stable when exposed to air, and the calcium and strontium salts are also crystalline. All these salts when heated at about 300° give off alcohol and are converted into pyrophosphates, but their solutions are stable, and are not affected by prolonged ebullition. The calcium salt, unlike the corresponding phosphate, is not partially decomposed by water, and its aqueous solution remains neutral and yields no precipitate when boiled.

C. H. B.

Chlorination of Ether. By P. FRITSCH and W. SCHUMACHER (*Annalen*, 279, 301—310; compare this vol. i, 483).—When chlorine is passed into cooled ether, the first product is monochlorether, which cannot, however, be obtained in the pure state, as it decomposes very rapidly on distillation. The final product of the action of chlorine on ether at 15° , when distilled under diminished pressure, yields two main fractions, one of which boils at $80\text{--}81^\circ$, and the other at $102\text{--}103^\circ$, under a pressure of 100 mm. The first consists chiefly of dichlorether, the second of trichlorether; but neither is pure, and cannot be obtained pure even by repeated distillation, as a certain amount of decomposition always occurs.

Dichlorether is readily decomposed by water at the ordinary temperature (compare Abeljanz, *Annalen*, 164, 222), and, if the hydrochloric acid be removed by digestion with marble, 90 per cent. of the theoretical amount of monochloraldehyde alcoholate is obtained. On distillation, this substance decomposes into monochloraldehyde, water, and monochloroacetal; $2\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OEt})\cdot\text{OH} = \text{CH}_2\text{Cl}\cdot\text{CHO} + \text{H}_2\text{O} + \text{CH}_2\text{Cl}\cdot\text{CH}(\text{OEt})_2$. It may advantageously be used for the preparation of monochloraldehyde, which is formed to the extent of 90 per cent. of the theoretical yield, when the alcoholate is heated with anhydrous oxalic acid. When it is treated with alcohol, the alcoholate yields monochloroacetal. If methylic alcohol be added, a mixture of the dimethyl- and diethyl-acetals is obtained, and not a mixed acetal.

Trichlorether is only very slowly attacked by cold water, yielding

dichloraldehyde alcoholate; on distillation, this decomposes into dichloraldehyde hydrate and dichloroacetal, but not so sharply as the monochloro-compound. Dichloraldehyde alcoholate may also be employed for the preparation of dichloraldehyde and dichloroacetal.

A. H.

Cholesterol. By J. MAUTHNER and W. SUIDA (*Monatsh.*, 15, 362—374).—A great number of analytical results obtained by the authors with cholesterol and its derivatives, seem to show that the composition of cholesterol is expressed by the formula $C_{27}H_{44}O$.

The compound obtained by treating trichlorocholestone with zinc-dust and acetic acid, and also by the action of zinc acetate on cholesteryl chloride, is found to be cholesteryl acetate. Cholesteryl propionate and butyrate may be obtained from cholesteryl chloride in a similar way. The propionate melts at 97—98°. E. C. R.

A Polymeride of Epichlorhydrin. By E. PATERNO and V. OLIVIERI (*Gazzetta*, 24, i, 305—309).—Epichlorhydrin (200 c.c.) is slowly added to concentrated hydrofluoric acid (20 c.c.) contained in a platinum vessel; after 24 hours' repose, the product is rendered slightly alkaline by the addition of sodium carbonate, and any excess of epichlorhydrin is carried away by a current of steam. The residual oil, which is more viscous than glycerol, is a *polymeride* of epichlorhydrin; it has a piquant odour, is heavier than water, and dissolves in alcohol, benzene, ether, or acetic acid. It decomposes at 200° when distilled under diminished pressure, and gives anomalous depressions of the boiling point of benzene. No oxime or hydrazone could be prepared, but the substance is acted on by acetic chloride or anhydride. It also yields a *product* resembling cellulose, when heated at 200° with very dilute sulphuric acid; this substance, however, could not be isolated in a pure state. W. J. P.

Behaviour of Various Sugars towards Pure Yeast Cultures.—By E. FISCHER and H. THIERFELDER (*Ber.*, 27, 2031—2037).—No systematic attempt has hitherto been made to study the behaviour of synthetical sugars towards pure cultures of yeast. The authors, following this line of investigation, have also reopened the study of a few natural sugars, employing in their experiments the following twelve varieties of yeast: *Saccharomyces pastorianus*, I, II, III; *S. cerevisiae*, I; *S. ellipsoideus*, I, II; *S. marxianus*; *S. membranefaciens*; *S. productivus*; and three forms known as "brewery yeast," "distillery yeast," and "milk-sugar yeast" respectively. Repetition of previous experiments has invariably led to the confirmation of recorded conclusions, except in the case of sorbose, which is not attacked by pure cultures.

The experiments were carried out in a flask of about 1 c.c. capacity, into the neck of which a small U-tube is fitted. The flask having been two-thirds filled with a mixture of yeast extract containing citric acid, and a 20 per cent. solution of the sugar under examination, the liquid is sterilised, and 0.013 gram of the pure culture introduced; the U-tube containing baryta water is then fitted into the neck of the flask, special attention being paid to the security of the joint. The

whole apparatus is then allowed to remain at 24—28° for a period of from 3 to 10 days.

The authors have succeeded in tracing a connection between the molecular configuration of a sugar and its behaviour towards ferments, pointing out that whilst grape-sugar and *d*-mannose are readily fermentable, a selective capacity is displayed by the cultures towards *d*-galactose and *d*-talose, the former being only slowly attacked by some yeasts, *d*-talose escaping altogether. The delicacy of this discrimination between geometrical modifications is rendered more striking by the fact that such widely dissimilar molecular arrangements as glycerose and mannose are broken down by these organisms; it seems probable that the yeasts attack with most readiness those sugars whose molecular configuration resembles most closely that of grape sugar.

In addition to the sugars already mentioned, it is found that the cultures have no action on *l*-mannose, *l*-gulose, *l*-arabinose, rhamnose, α -glucoheptose, or α -glucooctose. Representatives of the glucosides recently described by E. Fischer (this vol., i, 3) have been included in the experiments, with the result that whilst *S. pastorianus* I, "brewery yeast," and "distillery yeast" induce fermentation in solutions of methyl- and ethyl-glucosides, no action is set up in the case of glucose-resorcinol, glucose-pyrogallol, or glucose-ethylmercaptol; this cannot be accounted for by the liberation of the aromatic residue and its subsequent action on the yeast, the latter preserving for many days its activity in a solution of grape sugar.

It was thought possible that by allowing growing yeast to remain for some months in contact with an in fermentable sugar, the yeast in question might develop a fermentative capacity for that sugar; an experiment in this direction, however, led to a negative result.

M. O. F.

Action of Paraformaldehyde (Trioxymethylene) on Alcohols in presence of Ferric Chloride. By A. TRILLAT and R. CAMBIER (*Compt. rend.*, 118, 1277—1280).—When a mixture of paraformaldehyde and an alcohol in molecular proportion is boiled for a few hours with from 1 to 4 per cent. of anhydrous ferric chloride, an action takes place in accordance with the general equation $(CH_2O)_x + 6ROH = 3CH_2(OR)_2 + 3H_2O$. The products, which are obtained in considerable quantity, are colourless liquids with a very agreeable odour; the higher terms are insoluble in water, but form hydrates. They boil undecomposed under ordinary pressure. The propyl compound and its higher homologues dissolve sulphur and iodine. All the derivatives are violently oxidised by nitric acid, and react energetically with chlorine and bromine. Sulphuric acid decomposes them with regeneration of paraformaldehyde. Their characteristic reaction is the formation of coloured products with dimethylaniline in presence of an acid and an oxidising agent.

Methylal is readily obtained by this method from paraformaldehyde and methylic alcohol. The ethyl compound is obtained as a hydrate, $CH_3(OEt)_2 \cdot H_2O$ boiling at 74—75°; sp. gr. at 16° = 0.8338; 1 part dissolves in 15 parts of water at 20°. The normal propyl compound has an odour of pine apple, and boils at 136°; sp. gr. at 14° =

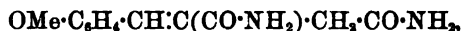
0·8319. Its hydrate, with $1\text{H}_2\text{O}$, boils at 90° ; sp. gr. at $14^\circ = 0\cdot8661$. The isopropyl compound is obtained as a monhydrate which boils at $79\text{--}80^\circ$; sp. gr. at $14^\circ = 0\cdot8362$. The isobutyl compound boils at 164° ; sp. gr. at $14^\circ = 0\cdot8302$. Its monhydrate boils at 96° ; sp. gr. at $14^\circ = 0\cdot8491$. The isoamyl compound boils at 206° ; sp. gr. at $14^\circ = 0\cdot8391$; its monhydrate boils at about 98° . The hexylic compound boils at $174\text{--}175^\circ$; sp. gr. at $15^\circ = 0\cdot8223$. The caprylic compound boils at 289° , and is almost odourless; sp. gr. at $15^\circ = 0\cdot8477$. The allyl compound has a pungent odour, and boils at $138\text{--}139^\circ$; sp. gr. at $14^\circ = 0\cdot8948$; it forms a hydrate. The glycol compound, $\text{CH}_2(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_n$, has a pungent odour, and boils at $74\text{--}75^\circ$; sp. gr. at $25^\circ = 1\cdot0534$. With dimethylaniline, it gives the benzhydrol reaction. The propylglycol compound has a pleasant odour, and boils at 90° .
C. H. B.

Condensation of Aldehydes with Cyanides. By C. BECHERT (*J. pr. Chem.*, [2], 50, 1—28; compare Abstr., 1892, 1086).—*Methylenedisuccinimide*, $\text{CH}_2[\text{N}(\text{CO})_2\text{C}_2\text{H}_4]_2$, is produced by the action between paraformaldehyde and ethylenic cyanide in glacial acetic acid, in the presence of strong sulphuric acid; it crystallises in monoclinic pyramids, and does not melt at 270° . Chromic and nitric acids are without action on the compound; nitrous acid has very little action on it, and bromine only attacks it when heated with it in presence of water; when it is distilled with dilute sulphuric acid, formaldehyde passes over, and succinic acid remains in the retort.

The interaction of ethylenic cyanide with benzaldehyde in alcohol at 0° , in presence of sodium ethoxide, yields a compound, $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2$, which crystallises in yellow needles, melting at 214° ; its behaviour with hydrochloric acid indicates that it is a product of the condensation of 2 mols. of ammonia (produced from the ethylenic cyanide) with 3 of benzaldehyde.

When the action between ethylenic cyanide, benzaldehyde, and sodium ethoxide proceeds at 50° , *a*-benzal- β -cyanopropionamide, $\text{CN}\cdot\text{CH}_2\cdot\text{C}(\text{CHPh})\cdot\text{CO}\cdot\text{NH}_2$, is produced. This crystallises from hot glacial acetic acid in white needles, carbonises at 260° , and is insoluble in most solvents.

Paramethoxybenzalsuccinamide,



is formed on adding a hot solution of sodium ethoxide to a solution of ethylenic cyanide and anisaldehyde in alcohol; it crystallises in white needles, melts at 255° , and dissolves in alcohol and glacial acetic acid, but not in water or ether. It is feebly basic, yielding a nitrate, $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_5\cdot\text{HNO}_3$, which crystallises in yellow needles, and melts at 181° , and a hydrochloride, $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_5\cdot\text{HCl}$, which forms yellow needles melting at 240° .

Ethylic paramethoxyphenyl- α -cyanacrylate,



the condensation product from ethylic cyanacetate and anisaldehyde, in presence of sodium ethoxide in alcoholic solution, forms pale

yellow, triclinic crystals, melts at 85°, and dissolves in alcohol, ether, chloroform, and benzene. The corresponding *acid* crystallises in yellow needles, and melts at 226°; its *potassium* and *silver* salts were prepared, and the behaviour of the former with several of the usual precipitants is recorded. The ethylic salt, when treated with bromine in chloroform, yields the *bromo-derivative*,



it crystallises in white needles, and melts at 185°. The acid does not yield this derivative.

Ethylic cinnameryl- α -cyanacrylate, $\text{CHPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}(\text{CN}) \cdot \text{COOEt}$, from cinnamaldehyde and ethylic cyanacetate in presence of sodium ethoxide, crystallises in yellow needles, melting at 114°. The corresponding *acid* forms red flocks, and melts at 196°; the *potassium* salt and some of its reactions, and the *silver* salt, are described. The ethylic salt yields the *bromo-derivative*,



which crystallises in white laminæ, and melts at 95°; the corresponding derivative of the acid could not be prepared.

Ethylic furfur- α -cyanacrylate, $\text{C}_4\text{OH}_2 \cdot \text{CH} \cdot \text{C}(\text{CN}) \cdot \text{COOEt}$, is prepared in a similar manner; it crystallises in white needles, melts at 94°, and dissolves in chloroform and alcohol. The corresponding *acid* crystallises in yellow needles, and melts at 218°. When the ethylic salt is brominated in glacial acetic acid, the *bromo-derivative*, $\text{C}_4\text{OH}_2 \cdot \text{CBr} \cdot \text{C}(\text{CN}) \cdot \text{COOEt}$, is obtained; it crystallises in yellow needles, and melts at 111°. The acid yields no *bromo-derivative*.

Ethylic methylenedioxyphenyl- α -cyanacrylate,



the condensation product formed from piperonal and ethylic cyanacetate in presence of sodium ethoxide, forms yellow laminæ, melting at 106°; the corresponding *acid* crystallises in yellow needles, and melts at 230°. The *bromo-derivative*,

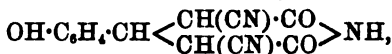


forms yellow crystals, melting at 131°.

Ethylic orthohydroxybenzaldehydicyanacetate,



prepared in like manner from ethylic cyanacetate and salicylaldehyde, forms white, hard, granular crystals, melts at 140°, and dissolves in the usual solvents. Its constitution is confirmed by the fact that, on treatment with ammonia, it yields the *imide*,



which crystallises in laminæ, does not melt at 280°, and is insoluble, except in glacial acetic acid. The *potassium* and *silver* salts of the corresponding acid were prepared, but when the yellow solution of the former is mixed with dilute sulphuric acid, a crystalline precipitate of *cyanocoumarin*, $\text{C}_6\text{H}_4 \cdot \begin{array}{c} \text{O} \\ \text{CH} \cdot \text{C}(\text{CN}) \end{array} \text{CO}$, is formed instead of

the free acid. This neutral substance melts at 182° , and gives no violet coloration with ferric chloride in alcoholic solution, showing that the salicylic hydroxyl no longer exists in the molecule; its constitution is further settled by the fact that it yields coumarincarboxylic acid (m. p. 187°) on hydrolysis. The same acid may be produced by the direct hydrolysis of ethylic orthohydroxybenzaldicyanacetate; its *barium* salt and *amide* (m. p. 236°) were prepared. With bromine, ethylic orthohydroxybenzaldicyanacetate yields a bromo-derivative, $C_{11}H_8NO_3Br$, as an orange-red crystalline powder, melting between 125° and 128° .
A. G. B.

Chlorination of Acetone. By P. FRITSCH (*Annalen*, 279, 310—319; compare Abstr., 1893, i, 303).—When acetone is chlorinated in the usual way, the first product obtained has the boiling point ascribed to monochloracetone, but contains about 4 per cent. of chlorine less than is required for this substance, the deficiency being probably due to the presence of mesityl oxide, formed by the action of the accumulated hydrogen chloride on the excess of acetone. This impurity may be avoided by introducing 1 part of marble for every 4 parts of acetone into the chlorinating flask, and gradually dropping in $2\frac{1}{2}$ parts of water. The product thus obtained has the theoretical composition, boils at 118 — 120° , and has a sp. gr. of 1.154 at 15° .

The further chlorination of acetone, carried out in the same manner in diffused daylight, gave a product consisting of monochloracetone mixed with both asymmetric and symmetric dichloracetone. The last of these, which has not previously been recognised among the products of the direct chlorination of acetone (*Annalen*, 208, 355; *Ber.*, 7, 467), is found in the fraction which boils at 167 — 172° , and is formed to the extent of about 10 per cent. of the whole.

For the preparation of pentachloracetone, pure monochloracetone, or the crude mixture of mono- and di-chloracetone, may be used. The substance may thus be obtained in the pure state, free from condensation products or their chlorine substitution derivatives. Pentachloracetone has a sp. gr. of 1.69 at 15° , whereas, according to Cloëz (*Ann. Chim. Phys.*, [6], 9, 189), who has also prepared it by direct chlorination, its sp. gr. is 1.576.
A. H.

Action of Ethylenediamine on Dicarboxylic acids. By F. ANDERLINI (*Gazzetta*, 24, i, 397—401).—Ethylenediamine succinate melts and decomposes at 195° , not at the lower temperature given by Mason (*Trans.*, 1887, 51, 10).

Ethylenediamine malate, $C_2H_3(OH)(COOH)_2(NH_2)_2C_2H_4$, is obtained by the action of malic acid on ethylenediamine; it forms small, colourless crystals, melting and decomposing at 198° .

The *phthalate* and *fumarate* are white, crystalline powders; they melt at 225 — 227° and 210° respectively, and at the same time undergo decomposition; the *maléate* was also prepared.
W. J. P.

Action of Ethylenediamine on Anhydrides of Bibasic acids. By F. ANDERLINI (*Gazzetta*, 24, i, 401—407; compare this vol., i,

375).—Ethylenediamine and maleic anhydride in benzene solution combine to form an additive compound, $C_2H_4(NH_2)_2 \cdot C_4H_2O_3$; it is a white, deliquescent powder, melting and decomposing at $90-110^\circ$.

The additive product of ethylenediamine and succinic anhydride is similar in appearance to the preceding; it melts and decomposes at about 120° , and resolidifies at $130-140^\circ$. This behaviour is due to the formation of *succinylethylenediamine*, $C_2H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > C_2H_4$, a white, hygroscopic substance, melting at $160-170^\circ$.

Phthalic anhydride also yields a similar additive product with ethylenediamine; on boiling with benzene, water is eliminated, and *phthalylethylenediamide*, $C_2H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > C_2H_4$, is formed. The latter is a voluminous, white, hygroscopic powder, melting at 125° .

Diphthalylethylenediimide, $C_6H_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} > N \cdot CH_2 \cdot CH_2 \cdot N \begin{smallmatrix} \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{smallmatrix} > C_6H_4$, is obtained by heating phthalic anhydride and ethylenediamine in benzene solution at 100° ; it crystallises in colourless needles, melting at $243-244^\circ$, and distils without decomposing. W. J. P.

Oxidation of Normal Fatty Acids. By R. MARGULIES (*Monatsh.*, 15, 273—275).—The purity of the acids employed was proved by a determination of the boiling point and by the method of fractional saturation. Potassium permanganate was employed as the oxidising agent, both in acid solution and in alkaline. Acetic acid was found to be the most difficult to oxidise, and of the other fatty acids, those of higher molecular weight are more easily oxidised.

Acetic acid, in the presence of excess of sodium carbonate, yields carbonic and oxalic acids. In the presence of sulphuric acid, it yields only carbonic acid.

Propionic acid in alkaline solution yields oxalic acid; in acid solution, acetic acid.

Normal butyric acid in alkaline solution yields oxalic and acetic acids; in acid solution only acetic acid. Propionic acid could not be detected in the product. When oxidised with sodium peroxide in the cold, it yields acetic acid, and a small quantity of formic acid.

Normal heptylic acid, in alkaline solution, yields oxalic, acetic, and formic acids; in acid solution, acetic and traces of formic acid.

E. C. R.

Action of Ammonium Hydrosulphide on Dichloroacetic acid. By C. BÖTTINGER (*Arch. Pharm.*, 232, 244—248).—Dichloroacetic acid (5 grams) is neutralised with ammonia, the solution cooled and mixed with saturated ammonium hydrosulphide solution (35 c.c.); after 60 hours, the mixture is evaporated on the water bath to expel excess of ammonium hydrosulphide, water is added and the solution is fractionally precipitated with lead acetate. The acids recovered from the first fraction consist of oxalic acid and the acid $C_2H_2SO_2 + H_2O$, which forms crystals, melts at $88-89^\circ$, and is much more soluble in water and in ether than oxalic acid is; the lead salt, the silver salt, and a few reactions of the acid are described.

The acids from the second fraction appear to consist of glycollic acid and the above thio-acid. A. G. B.

Derivatives of Ethylic Cyanacetate and Ethylic Cyano-succinate. By L. BARTHE (*Compt. rend.*, 118, 1268—1271).—Ethylic β -bromopropionate is obtained by saturating cooled acraldehyde with gaseous hydrogen bromide, oxidising the bromaldehyde, and converting the acid into the ethylic salt.

When ethylic sodiocyanacetate is heated for some time with ethylic β -bromopropionate in presence of ethylic alcohol, *ethylic cyanoglutarate*, $\text{COOEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$, is formed; it boils at 198° under a pressure of 50 mm.

Ethylic dimethylcyanosuccinate, $\text{COOEt}\cdot\text{CMe}_2\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$, is a colourless, oily liquid, boiling at 186.5° . It is readily obtained in considerable quantity by the action of ethylic bromisobutyrate on ethylic sodiocyanacetate in presence of absolute alcohol. When boiled with methylic iodide, no action takes place.

No condensation takes place when ethylic bromiosuccinate is boiled with ethylic sodiocyanosuccinate, or heated with it in sealed tubes at 125° .

When ethylic β -cyanotricarballylate in alcoholic solution is heated for some time at 110 — 120° with dilute hydrochloric acid, it yields ammonium chloride, and tricarballylic acid. *Methylic tricarballylate* is obtained by mixing a solution of methylic cyanotricarballylate in methylic alcohol with a quantity of the same alcohol saturated with hydrogen chloride, and allowing the mixture to remain in a cool place for many months. It is a colourless, oily liquid, soluble in alcohol, but insoluble in alkalis; it boils at 228° under a pressure of 45 mm. C. H. B.

Ricinoleic acid, Ricinelaïdic acid, and Ricinostearolic acid. By C. MANGOLD (*Monatsh.*, 15, 307—315).—Ricinoleic acid distils under 50 mm. pressure at 250° , leaving a dark viscous residue in the retort. The distillate, which has the composition $\text{C}_{18}\text{H}_{32}\text{O}_2$, is a colourless oil at ordinary temperatures, but solidifies in a freezing mixture; it gives a barium salt which is insoluble in alcohol.

Ricinelaïdic acid is obtained by treating castor oil with sodium hydroxide and pouring the mixture into warm dilute hydrochloric acid. The product is then washed with water and treated with dilute nitric acid and potassium nitrite. It crystallises from light petroleum in white crystals, and melts at 51° ; when distilled under 15—30 mm. pressure, it boils at 240 — 250° , but at the same time decomposes, being converted into a new acid of the composition $\text{C}_{18}\text{H}_{32}\text{O}_2$. This crystallises in lustrous, white tablets, and melts at 53 — 54° . The ammonium salt crystallises in lustrous leaflets and is sparingly soluble in cold water. The tetrabromo-compound,



crystallises in white nodules and melts at 80 — 81° .

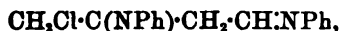
Ricinelaïdic acid, when reduced with red phosphorus and iodine, and then with zinc and hydrochloric acid, is converted into stearic acid.

Ricinelaidic hydrazide, $\text{OH}\cdot\text{C}_{17}\text{H}_{33}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, is obtained by heating the acid with phenylhydrazine at 120° . It crystallises in tufts of slender white needles, and melts at $110\text{--}110.5^\circ$.

Ricinostearolic acid, $\text{C}_{18}\text{H}_{34}\text{O}_2$, is obtained by brominating pure castor oil and boiling the product with alcoholic potash; it melts at 51° . The *barium* salt crystallises from alcohol in beautiful silky leaflets. When the acid is treated with concentrated sulphuric acid, it is converted into hydroxystearoricinic acid. This separates in white crystals and melts at $78\text{--}80^\circ$.
E. C. R.

Derivatives of Glycollic Acid. By C. A. BISCHOFF and P. WALDEN (*Annalen*, 279, 45—70).—The compound melting at 220° , and hitherto known as glycollide, is in reality a polymeride; it is best obtained by Norton and Tscherniak's method (*Bull. Soc. Chim.*, 30, 102), namely by heating sodium chloracetate at 150° , preferably with petroleum (b. p. $150\text{--}200^\circ$). When distilled under diminished pressure, it is converted into *glycollide*, which crystallises in large plates, melts at $86\text{--}87^\circ$, and is shown by the cryoscopic method to have the formula $\text{CH}_2\langle\begin{smallmatrix}\text{CO}\cdot\text{O} \\ \text{O}\cdot\text{C}\end{smallmatrix}\rangle\text{CH}_2$. Attempts to prepare glycollide by direct distillation of sodium chloracetate under diminished pressure did not yield favourable results. Glycollide may also be obtained by distilling sodium bromacetate or glycollic acid under diminished pressure (compare Abstr., 1893, i, 250; Anschütz, *ibid.*, 306). Glycollide dissolves in hot water with partial conversion into the polymeric compound, but when the aqueous solution is boiled for several hours, glycollic acid is formed.

Glycollic anilide, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, is obtained by boiling glycollide, polyglycollide, or glycollic acid with aniline; it crystallises in prisms (see *Zeit. Kryst. Min.*, 21, 104) and melts at 97° . The authors failed to obtain the acicular modification (m. p. 108°) described by Norton and Tscherniak (*Ber.*, 12, 285). *α-Dichloro-β-anil-acetoacetanilide chloride*, $\text{CH}_2\text{Cl}\cdot\text{C}(\text{NPh})\cdot\text{CHCl}\cdot\text{CCl}\cdot\text{NPh}$, is obtained by treating glycollic anilide with phosphorus pentachloride; it crystallises from acetone in yellow needles, commences to decompose at 209° , and is identical with the compound obtained by Wallach from chloracetanilide and phosphorus pentachloride (*Annalen*, 184, 97). If treated with alcoholic soda, a base, $\text{NPh}\cdot\text{C}\langle\begin{smallmatrix}\text{CHCl} \\ \text{CHCl}\end{smallmatrix}\rangle\text{C}\cdot\text{NPh}$, is obtained, which crystallises in almost colourless needles, and melts at $133\text{--}134^\circ$; this, by treatment with concentrated hydrochloric acid, is reconverted into the original substance. The latter, when reduced with zinc dust and acetic acid, gives a compound,

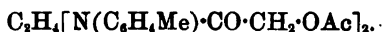


melting at 172° , and when reduced in alkaline solution a non-chlorinated derivative is formed.

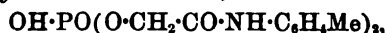
Dichloroacetanilide, $\text{CHCl}_2\cdot\text{CO}\cdot\text{NHPh}$, (m. p. $116\text{--}117^\circ$) is obtained by treating chloracetanilide with phosphorus pentachloride; chloracetanilide, $\text{CH}_2\text{Cl}\cdot\text{CONHPh}$, is produced when glycollic anilide is dissolved in phosphorus oxychloride and the solution is treated with

phosphorus pentachloride, the liquid portion distilled under diminished pressure, and the residue extracted with hot water. *Phosphoric triglycollic anilide*, $\text{PO}(\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh})_3$, is formed by treating glycollic anilide in a variety of ways with phosphorus pentachloride or phosphorus oxychloride; this compound is precipitated on adding water to the product, which must not be distilled. It forms colourless needles, melts at 196° , and dissolves in hot soda undergoing partial decomposition. The ultimate product of the action of phosphorus pentachloride (5 mols.) on glycollic anilide is oxanilide.

Glycollic orthotoluidide, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, is prepared from polyglycollide, or glycollic acid, and orthotoluidine; it crystallises in long needles and melts at 67° . The compound (m. p. $188\text{--}189^\circ$) previously described as glycollic orthotoluidide (Abstr., 1890, 1161) is probably diacetylglycolylethylenediorthotolyldiamine



Phosphoric diglycollic orthotoluidide,



is formed by shaking glycollic orthotoluidide dissolved in dry chloroform with the calculated quantity of phosphorus pentachloride; it melts at $168\text{--}170^\circ$. *Phosphoric triglycollic orthotoluidide*,

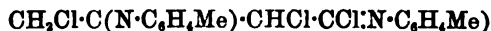


is formed, on allowing the last-mentioned reagents to remain together for 12 hours; it melts at 143° . *Chloracetylorthotoluidide*,



is obtained by treating with water the chloroform filtrate from the last-described compound; it melts at $111\text{--}112^\circ$, and has been described by Abenius and Widman (*J. pr. Chem.*, [2], 38, 299).

Glycollic paratoluidide, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, melts at 143° . When treated with phosphorus pentachloride α -dichloro- β -paratolyl-acetoaceticparatoluidoimidochloride,



is formed; it sinters at 270° , and is converted into the compound,



when heated with alcoholic soda; this melts at 133° .

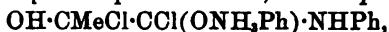
Phosphoric triglycollic paratoluidide, $\text{PO}(\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_3$, melts at 188° ; chloracetylparatoluidide (P. Meyer, *Ber.*, 8, 1154) melts at $161\text{--}162^\circ$. Oxalic paratoluidide (m. p. 263°) is the ultimate product of the action of phosphorus pentachloride on glycollic paratoluidide. Other compounds which were not properly identified are also obtained by the action of phosphorus pentachloride on glycollic paratoluidide.

Glycollic α -naphthalide, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, melts at 128° , and gives acet- α -naphthalide (m. p. 159°) when heated with acetic acid.

Glycollic β -naphthalide, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, melts at 138° and yields aceto- β -naphthalide (m. p. 132°) when heated with acetic anhydride.

Phosphoric triglycollic β -naphthalide $\text{PO}(\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)_3$,
melts at 192—196°. A. R. L.

Derivatives of Lactic acid. By C. A. BISCHOFF and P. WALDEN (*Annalen*, 279, 71—99).—Lactide, $\text{CHMe}\langle\begin{smallmatrix}\text{CO}\cdot\text{O} \\ \text{O}\cdot\text{CO}\end{smallmatrix}\rangle\text{CHMe}$, contains two asymmetrical carbon atoms in its molecule, and should, therefore, exist in other modifications. The authors have prepared lactide by heating ordinary inactive lactic acid or sodium α -bromopropionate (see Abstr., 1893, i, 250), but found that with the exception of oily bye-products, the ordinary lactide (m. p. 124.5°) alone was obtained; unlike glycolide (last abstract), it does not polymerise. When heated with aniline, lactanilide (Leipen, Abstr., 1888, 580) is formed; the latter yields acetanilide when heated with acetic anhydride, and, if treated with phosphorus pentachloride, the compound,



is obtained, which melts at 79—82°, and decomposes into pyruvic anilide when dissolved in hot water.

Pyruvic anilide is also obtained directly from lactanilide when it is warmed with phosphorus pentachloride; in addition to the properties described by Nef (Abstr., 1892, 1440; compare also Abstr., 1893, i, 511), it is observed that the compound decomposes at 252°.

α -Chloropropanilide, $\text{CHMeCl}\cdot\text{CO}\cdot\text{NHPh}$, is obtained by treating a solution of lactanilide in benzene with phosphorus pentachloride. It forms colourless plates, and melts at 92°.

Phosphoric trilactanilide, $\text{PO}(\text{O}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NHPh})_3$, is one of the products obtained when lactanilide is heated with phosphorus pentachloride, but it is best prepared by the action of phosphorus pentachloride on a solution of the anilide in phosphorus oxychloride; it melts at 205°.

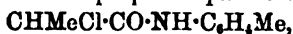
Lactic orthotoluidide melts at 75—76° (compare Leipen, *loc. cit.*), and yields pyruvic orthotoluidide when warmed with phosphorus pentachloride; this dissolves in aqueous sodium hydroxide, and on acidifying the solution, a polymeride, $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4$, melting at 177°, separates. The compound (m. p. 111°) formerly regarded as a hydrated orthotoluidide (Abstr., 1893, i, 511) is in reality a chlorinated compound, $\text{C}_{10}\text{H}_{11}\text{NClO}$; it is formed by boiling lactanilide with benzene and phosphorus pentachloride.

Phosphoric trilactic orthotoluidide, $\text{PO}(\text{O}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_3$, melts at 177°.

Lactic paratoluidide melts at 107° (compare Leipen, *loc. cit.*); if treated with phosphorus pentachloride, it is converted into pyruvic paratoluidide, $\text{C}_{10}\text{H}_{11}\text{NO}_2$, which melts at 109°. When a solution of the latter in alkalis is acidified, a polymeric compound, $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4$, melting at 207°, is obtained.

Phosphoric trilactic paratoluidide, $\text{PO}(\text{OCHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_3$, melts at 156°.

When lactic paratoluidide is heated with phosphorus pentachloride, the product distilled in a vacuum, and the residue fractionally crystallised from alcohol, α -chloropropionic paratoluidide,



melting at 124°, and α -dichloropropionic paratoluidide,



melting at 84—86°, are obtained.

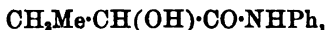
Lactic methylanilide, $\text{OH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NMePh}$, prepared by heating lactide or lactic acid with methylaniline, melts at 95—96°; when treated with phosphorus pentachloride, it yields a mixture consisting principally of oily substances.

Glyceric paratoluidide, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, melts at 120—122°, and differs from the analogous compounds, containing but one hydroxyl group in that it dissolves in cold alkalis.

Lactic α -naphthalide, $\text{OH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$, melts at 108°, and decomposes into its proximate constituents when heated with acetic anhydride; the benzoyl derivative melts at 155°. By the action of phosphorus pentachloride on the α -naphthalide, there are obtained—*pyruvic α -naphthalide*, $\text{COMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$, which melts at 102—103°, and yields a *polymeride* melting at 202—203°; and *phosphoric trilactic α -naphthalide*, $\text{PO}(\text{O} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7)_3$, melting at 166—169°.

Lactic β -naphthalide, $\text{OH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$, melts at 137·5°, and behaves with acetic anhydride in a manner analogous to the α -derivative; the *benzoyl* derivative melts at 177°. A. R. L.

Derivatives of the two α -Hydroxybutyric acids. By C. A. BISCHOFF and P. WALDEN (*Annalen*, 279, 100—118).— α -Hydroxybutyric acid is best prepared by heating α -bromobutyric acid with a solution of potassium carbonate (1 mol.). It boils at 140° under a pressure of 14 mm., and the chief portion distils at 225° under a pressure of 764 mm., being meanwhile converted into the lactide, so that the whole does not pass over until a temperature of 260° is attained (see also Markovnikoff, *Annalen*, 119, 115; 120, 279; 153, 242). The lactide has already been described (*Abstr.*, 1893, i, 251). The following derivatives are obtained by heating the acid or the lactide with the corresponding bases at 180°. The *anilide*,



melts at 90°; the *orthotoluidide* at 57°; and the *paratoluidide* at 112—113°. When the latter is treated with phosphorus pentachloride in chloroform solution, it yields *propionylformoparatoluidide*, $\text{CH}_3\text{Me} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, which forms monoclinic crystals, and melts at 130—131°; if dissolved in alkali and reprecipitated with acid, a polymeride melting at 192°, probably $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4$, is obtained. The yield of the α -naphthalide, which melts at 96°, is small; whilst by heating α -hydroxybutyric acid with β -naphthylamine, $\beta\beta$ -dinaphthylamine (*Abstr.*, 1892, 1337) is produced, together with a small amount of the β -naphthalide melting at 126°.

Sodium α -bromisobutyrate, $\text{C}_4\text{H}_7\text{BrO}_2\text{Na} + \frac{1}{2}\text{H}_2\text{O}$, crystallises in colourless, microscopic needles; its behaviour on distillation is described (*Abstr.*, 1893, i, 251). When α -hydroxyisobutyric acid is treated with phosphorus pentachloride and the product distilled, carbonic anhydride is evolved, and aldehyde, acetone, acetic acid, and an unknown compound having the odour of camphor and boiling

at 150—155°, pass over. Neither by the method just described, nor by heating α -hydroxyisobutyric acid at 200—215°, was it found possible to prepare the lactide.

α -Hydroxyisobutanilide, $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NHPh}$, forms colourless, rhombic tables, and melts at 136°. When treated with phosphorus pentachloride, it yields a *hydrochloride*, $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NHPh}\cdot\text{HCl}$, melting at 113°, and decomposing into the anilide when boiled with water; besides this, α -chlorisobutanilide, $\text{CMe}_2\text{Cl}\cdot\text{CO}\cdot\text{NHPh}$, melting at 67—68°, is also formed. If α -hydroxyisobutanilide is dissolved in chloroform containing phosphorus oxychloride, and the solution treated with phosphorus pentachloride, an unstable compound is obtained which melts at 113°, and, when boiled with water or alcohol, decomposes yielding *phosphoric trihydroxyisobutanilide*,



melting at 158—159°.

α -Hydroxyisobutyric orthotoluidide, $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, melts at 88°, and, when treated with phosphorus pentachloride, yields *phosphoric trihydroxyisobutyric orthotoluidide*,



melting at 194—196°, and α -chlorisobutyric orthotoluidide,



melting at 56—59°.

α -Hydroxyisobutyric paratoluidide has been already described by Tigerstedt (Abstr., 1893, i, 53). *Phosphoric trihydroxyisobutyric paratoluidide* melts at 160—162°, and α -chlorisobutyric paratoluidide at 70°.

α -Hydroxyisobutyric naphthalide melts at 159—161°.

By the action of α -hydroxyisobutyric acid on β -naphthylamine, $\beta\beta$ -dinaphthylamine is not formed as in the case of α -hydroxypropyric acid, but α -hydroxyisobutyric β -naphthalide (Tigerstedt, *loc. cit.*) is obtained.

A. R. L.

Isosuccinic acid and Isomalic acid. By M. PUSCH (*Arch. Pharm.*, 232, 186—221).—The author finds that, contrary to the statements of Krestownikoff (this Journal, 1877, ii, 442), isosuccinic acid is the product of the reaction between ethylic α -bromopropionate and potassium cyanide, whether in alcoholic or aqueous solution. Isosuccinic acid melts at 134°, and is soluble in 1·1 parts of water at 17°; the solutions of its normal and acid alkali salts are precipitated by calcium chloride and barium chloride even when the dilution is 1 : 50, particularly on heating.

Ammonium ($1\text{H}_2\text{O}$) and *copper* ($3\text{H}_2\text{O}$) *isosuccinates* are described as being novel salts (compare Beilstein, [3], 1, 663), and the known salts have been prepared, the amount of water of crystallisation being in some cases corrected.

The author confirms the statements of Schmüger and of Brunner (Abstr., 1893, i, 145) as to the properties of isomalic acid. He has

also prepared Böttinger's "methyltartronic acid" (*Ber.*, **14**, 148), but finds that the product has the formula $C_4H_4O_6$, and is possibly hydroxycitraconic acid. The presence of a molecule of water of crystallisation appears to have misled Böttinger. A. G. B.

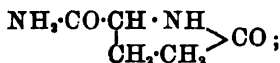
Derivatives of Glutamic acid. Pyroglutamic acids and Pyroglutamides. By A. MENOZZI and G. APPIANI (*Gazzetta*, **24**, i, 370—391; compare *Abstr.*, 1892, 298).—Haitinger (*Monatsh.*, **3**, 228) prepared inactive pyroglutamic acid by heating dextroglutamic acid at 180—190°; the authors find, however, that on heating dextroglutamic acid at 150—160°, water is evolved and *levopyroglutamic acid*, $\begin{array}{c} \text{COOH} \cdot \text{CH} \cdot \text{NH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CO}$, is formed. It is obtained in large, colourless, orthorhombic crystals melting at 162°;

$$a : b : c = 1.5034 : 1 : 1.6292.$$

In a 12.8 per cent. aqueous solution at 17°, it has the specific rotatory power $[\alpha]_D = -7.21^\circ$, and is more soluble in water than the inactive modification into which it is converted by heating at 180°. On boiling with barium hydroxide, it yields dextroglutamic acid.

Silver dextroglutamate, $C_5H_7NO_4Ag$, and *silver hydrogen dextroglutamate*, $C_5H_7NO_4Ag$, are white, insoluble powders.

The substance, which the authors have previously described as inactive glutimide, seems to have the constitution



it is *levorotatory*, the specific rotation for the anhydrous substance being $[\alpha]_D = -40^\circ$. When heated with alcoholic ammonia at 140—150°, or alone at 200°, it yields inactive pyroglutamide (Haitinger's glutimide); on boiling with caustic alkalis, it is converted into dextroglutamic acid. It yields a *hydrochloride*,



which crystallises in needles in the cold, but when boiled with hydrochloric acid, it gives dextroglutamic acid hydrochloride.

The authors have previously shown that on crystallising inactive glutamic acid from water, right- and left-handed enantiomorphous crystals are deposited; this fact could not be conveniently utilised for the preparation of the unknown *levoglutamic acid*, neither could the latter substance be prepared by crystallising the racemic modification with alkaloids. By cultivating *Penicillium glaucum* in solutions of the mixture, however, the dextro-acid was destroyed, and *levoglutamic acid* was left in solution. The *levo*-acid is in all respects similar to the dextro-acid, but the rotation is to the left, $[\alpha]_D = -12.9^\circ$, and the crystals possess the left-handed enantiomorphous form. It is of interest to note that whilst the dextro-acid has a characteristic taste, the *levo*-isomeride is almost tasteless.

Dextropyroglutamide is obtained by heating a solution of *levo*-glutamic acid in absolute alcohol saturated with hydrogen chloride,

and treating the ethylic salt with alcoholic ammonia; in a 3.3 per cent. aqueous solution, it has the specific rotation $[\alpha]_D = +41.29^\circ$, and has the same melting point and other properties as its lævo-isomeride. On boiling it with barium hydroxide, *dextropyroglutamic acid* is obtained; this has the specific rotation $[\alpha]_D = +7^\circ$ in a 2.6 per cent. aqueous solution, and is in all other respects similar to its lævo-isomeride.

In addition to the methods already given by the authors, inactive glutamic acid may be prepared by the following processes: by heating dextroglutamic acid at $160-170^\circ$ with barium hydroxide, and by heating inactive pyroglutamide with barium hydroxide or hydrochloric acid. The *ethylic* salt resembles its dextro-isomeride in appearance, but melts at 185° . On heating the acid at $150-160^\circ$, it is converted into inactive pyroglutamide; this substance, which may be prepared by a variety of methods, crystallises anhydrous, and melts at 214° . It yields a crystalline *hydrochloride*, and, on boiling with hydrochloric acid, gives inactive glutamic acid hydrochloride.

Inactive silver pyroglutamate, $C_6H_7NO_5Ag$, is obtained as a white, crystalline mass. On heating the free acid with barium hydroxide, inactive glutamic acid is obtained, whilst if treated with alcoholic ammonia, it yields inactive pyroglutamide; on passing hydrogen chloride into its alcoholic solution, inactive ethylic glutamate is obtained.

W. J. P.

Suberic, Azelaic, and Sebacic Anhydrides. By F. ANDERLINI (*Gazzetta*, 24, i, 474—477).—*Suberic anhydride*, $C_8H_{12} \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} > O$, is prepared by boiling suberic acid with acetic chloride; it is obtained as a crystalline, white powder melting at $62-63^\circ$, and is very soluble in benzene.

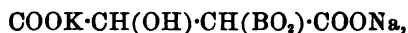
Azelaic anhydride, $C_9H_{14} \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} > O$, prepared from azelaic acid in the same manner, closely resembles the preceding anhydride, and melts at $52-53^\circ$. This process also affords a ready means of preparing sebacic anhydride.

W. J. P.

Emetics. By P. ADAM (*Compt. rend.*, 118, 1273—1275).—It is generally assumed that in the emetics the antimonious hydroxide, ferric hydroxide, or boric anhydride has a basic function, but Jungfleisch has advanced evidence to show that they really have an acid function. It is noteworthy that only acids which have a phenolic or alcoholic function form compounds with antimonious oxide, &c. Oxalic acid and phthalic acid, and their salts, do not combine with boric anhydride. In the preparation of the emetics, it is a salt of the acid that must be boiled with the antimony oxide or other oxides; as a rule, the free acid yields no such product. This is well seen in the case of boric anhydride, and mucic, saccharic, and salicylic acids, and their salts. The author has also obtained compounds of sodium lactate with boric anhydride, antimonious oxide, or arsenious oxide; of potassium malate with boric anhydride or antimonious oxide; of sodium potassium tartrate with 1 or 2 mols. of boric anhydride.

2 n 2

Further, lactic, malic, and tartaric acids prevent the precipitation of iron by alkali hydroxides, whereas this property is shown by none of the emetics, except the monoborotartrate,



which is the only one of these compounds which contains a hydroxyl group. With sodium potassium tartrate, arsenious oxide yields the same compound as with hydrogen potassium tartrate. Potassium hydrogen tartrate combines with 1 mol. only of boric anhydride, and the resulting compound prevents the precipitation of iron by alkali hydroxides.

Tartar emetic yields no precipitate with alkalis in the cold, unless the quantity of alkali added is equivalent to that already present in the salt. Litmus indicates neutrality when only one quarter of the alkali has been added, but phenolphthaleïn, cochineal, and turmeric indicate neutrality with the theoretical quantity of alkali. On the other hand, an imperfectly neutralised solution of tartar emetic deposits antimony oxide after some time. A freshly made solution, which is acid to litmus, becomes alkaline on dilution. When potassium carbonate is added to a solution of tartar emetic, there is immediate development of heat, but not immediate formation of a precipitate, and if a quantity of hydrochloric acid equivalent to the alkali is added, the solution still shows all the properties of tartar emetic. The decomposition of the emetic by alkalis proceeds slowly, like saponification.

The author concludes that the analogies and chemical behaviour of the emetics indicate that they are ethereal salts, and not double salts, the antimony and other oxides playing the part of acids.

C. H. B.

Emetics. By E. MAUMENÉ (*Compt. rend.*, 118, 1415—1418).—The author quotes analyses of tartar emetic and its analogues, with a view to show that the numbers obtained agree with the fractional formulæ deduced from his general law, and not with the usual simpler formulæ, in which the numbers of the atoms of the constituent elements are represented by simple whole numbers.

C. H. B.

Action of Nitrous acid on Trimethylenediamine. By N. DEMYANOFF (*J. Russ. Chem. Soc.*, 25, 677—679).—When the nitrite of trimethylenediamine is heated in aqueous solution on the oil-bath (see next abstract), and the gases evolved are passed through bromine, a bromide is obtained which corresponds with the hydrocarbon, C_3H_4 . The aqueous distillate contains allylic alcohol, and the residue a mixture of glycols, which boil chiefly at 200—210°. A glycol was isolated, the bromide of which had the composition $\text{C}_3\text{H}_4\text{Br}_2$.

J. W.

Action of Nitrous acid on Pentamethylenediamine. By DEMYANOFF (*J. Russ. Chem. Soc.*, 25, 665—677).—The hydrochloride of pentamethylenediamine was converted into the nitrite by means of

silver nitrite, and a 10 per cent. solution of the salt thus obtained was heated in an oil-bath until decomposition occurred. The gaseous products, on being passed through bromine, gave a bromide of the composition $C_6H_5Br_4$; this crystallises from alcohol in hexagonal plates, and melts at 86—87°.

From the water which distilled over, a red, oily layer separated on adding potassium carbonate, and this, on fractionation, yielded a glycol oxide, $C_6H_{10}O$, distilling between 82° and 87°, and a primary unsaturated alcohol of the same composition, which distilled between 133° and 136°, and had the sp. gr. 0.8533 at 18.5°/0°. The acetate boils at 145—146°, and has the sp. gr. 0.8137 at 19°/0°.

From the non-volatile residue, a mixture of glycols was obtained, boiling chiefly between 228° and 238°. The author succeeded in isolating from these pentamethylene glycol, by fractionation under reduced pressure. The corresponding bromide was found to boil at 208—214°, and had the sp. gr. 1.7017 at 16.5°/0°. J. W.

Action of Acetic Anhydride on Succinic acid in Presence of Calcium Chloride. By G. MAGNANINI and T. BENTIVOGLIO (*Gazzetta*, 24, i, 433—437; compare Magnanini, *Abstr.*, 1893, i, 623).—2 : 5 : 3-Dimethylacetylfurfuran, $\begin{matrix} \text{C}^{\text{Ac}}\text{CMe} \\ | \\ \text{CH} : \text{CMe} \end{matrix} > \text{O}$, is obtained by

heating a mixture of succinic acid, acetic anhydride, anhydrous sodium acetate, and zinc chloride for eight hours, in an autoclave at 200—205°. After distilling off the acetic anhydride and acetic acid, the residue is distilled in a current of steam, when the furfuran is obtained as a volatile oil, boiling at 193—196° under 760 mm. pressure. A small quantity of another oil is formed during the process. Dimethylacetylfurfuran readily absorbs bromine, and when heated with ammonia in a closed tube at 110—115°, yields 2 : 5 : 3-dimethylacetylpyrroline.

The *oxime*, $C_8H_{11}NO_2$, is prepared by heating dimethylacetylfurfuran with hydroxylamine hydrochloride, sodium carbonate, and dilute alcohol at 150°, in a closed tube. It crystallises in silvery scales, and melts at 78°. W. J. P.

The Benzene Nucleus. By W. VAUBEL (*J. pr. Chem.*, [2], 50, 58—60).—The author reconciles his formula for benzene (this vol., i, 326) with that of Kekulé. Baeyer's formula for limonene, which represents it as a $\Delta^{1,3}$ -dipentene (this vol., i, 252), is open to the objection that the optical activity of limonene is not accounted for by an asymmetrical carbon atom; the author gives a figure showing that a formula for limonene, constructed on the plan of his formula for benzene, does exhibit an asymmetrical carbon atom. A. G. B.

Action of the Electric Current on Benzene. By L. GATTERMANN and F. FRIEDRICHS (*Ber.*, 27, 1942—1943).—Renard (*Abstr.*, 1880, 802) has stated that an isobenzoglycol (m. p. 171°) is obtained by the action of an electric current on benzene, dissolved in alcohol containing dilute sulphuric acid. The authors have repeated the

experiments, and find that the compound produced is quinol (m. p. 169—170°).
E. C. R.

Condensation of Dichloroacetal with Benzene and Toluene.
By W. P. BUTTENBERG (*Annalen*, 279, 324—337; compare this vol., i, 520).—Diphenyldichlorethane, $\text{CHPh}_2\cdot\text{CHCl}_2$, is obtained by the condensation of dichloroacetal with benzene in the presence of sulphuric acid. It crystallises from hot alcohol in colourless prisms, melts at 80°, and distils and partially decomposes at 295—305°. Fuming nitric acid converts it into *dinitrodiphenyldichlorethane*, which crystallises from acetic acid in yellowish needles melting at 177—178°. Diphenyldichlorethane is converted by boiling alcoholic potash into *diphenylchlorethylene*, $\text{CPh}_2\cdot\text{CHCl}$, which crystallises from alcohol in long needles, melting at 42°, readily soluble in ether, &c.; it boils without decomposition at 298°. When heated with water at 200°, it is not converted into the corresponding aldehyde; on distillation with lime, it yields stilbene and other products. Fuming nitric acid converts it into a ketonic substance, which could not be obtained crystalline, but yielded a hydrazone; the latter melts at 234°, and has the composition of *dinitrobenzophenone hydrazone*, $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_4$.

When diphenylchlorethylene is heated with alcoholic sodium ethoxide, it yields *diphenylvinyl ethyl ether*, $\text{CPh}_2\cdot\text{CH}(\text{OEt})$, along with a little toluene. The former of these is a colourless, refractive liquid, boiling at 178—182° under a pressure of 18 mm. When diphenylvinyl ethyl ether is mixed with alcohol and treated with sulphuric acid, a hydrocarbon of the composition $\text{C}_{14}\text{H}_{10}$ is obtained, which separates from light petroleum in yellowish crystals melting at 157—158°. This substance does not yield a bromine additive compound, and was not further investigated.

Diphenylvinyl ethyl ether is readily converted by acids into diphenylacetaldehyde, the preparation of this substance being best carried out by saturating with hydrogen chloride a mixture of the diphenylvinyl ether with four times its volume of glacial acetic acid, and allowing it to stand. Diphenylacetaldehyde readily condenses with phenols to form products, which may be prepared by mixing the phenol with the diphenylvinyl ether and an acetic acid solution of hydrogen chloride. *Dihydroxytetraphenylethane*, $\text{CHPh}_2\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OH})_2$, is a red powder which melts at 230—232°. The *diacetate* crystallises in small needles and melts at 155°. *Dithymoldiphenylethane*, $\text{CHPh}_2\cdot\text{CH}(\text{C}_{10}\text{H}_{12}\cdot\text{OH})_2$, separates from acetic acid in colourless crystals melting at 224°. The *diacetate* forms needles melting at 152°. β -Naphthol does not behave in the normal way with diphenylacetaldehyde, but yields a substance of the formula $\text{C}_{24}\text{H}_{18}\text{O}$, which crystallises from alcohol in needles melting at 141—142°, has a molecular weight corresponding with the above formula, and does not give an acetate when heated with acetic chloride. It is possibly β -naphthodiphenyldihydrofurfuran, $\text{C}_{10}\text{H}_8\cdot\text{C}(\text{CH}_2)_2\text{CPh}_2$.

Diethylidichlorethane, $\text{CHCl}_2\cdot\text{CH}(\text{C}_6\text{H}_4\text{Me})_2$, is prepared in a manner similar to the diphenyl derivative; it is readily soluble in most solvents, crystallises in plates, and melts at 80°.

Ditolylchlorethylene, $\text{CHCl}:\text{C}(\text{C}_6\text{H}_4\text{Me})_2$, forms colourless needles melting at 67° . This compound is converted by sodium ethoxide into dimethyltolane, $\text{C}_6\text{H}_4\text{Me}:\text{C}:\text{C}:\text{C}_6\text{H}_4\text{Me}$, the *tetrachloride* of which forms asymmetric crystals and melts at 183° .

Dimethyltolane can readily be converted into deoxytoluoin, identical with that obtained by Stierlin (*Ber.*, 22, 383) from paramethylbenzaldehyde. The *oxime* of this substance crystallises in plates, and melts at 128° . When deoxytoluoin is treated in alcoholic solution with sodium amalgam, the product consists of *ditolylhydroxyethane*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Me}$, and the corresponding *pinacone*, $\text{C}_{12}\text{H}_{14}\text{O}_2$; the latter melts at 226° . Ditolylhydroxymethane, when warmed in acetic acid solution with a few drops of sulphuric acid, is converted, with loss of water, into paradimethylstilbene, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$.
A. H.

Iodosopseudocumene and Iodoxypseudocumene. By C. WILLGERODT (*Ber.*, 27, 1903—1905).—*Pseudocumylic iodochloride*, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{ICl}_2$ ($\text{Me}_3:\text{ICl}_2 = 1:2:4:5$), is obtained by passing chlorine into a well-cooled solution of iodosopseudocumene in chloroform or acetic acid, the latter giving the purest product. It separates from acetic acid in prisms which melt and decompose at 67 — 68° , and froth up rapidly at 70° . When treated with potassium or sodium carbonate, the iodochloride is converted into *iodosopseudocumene*, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{IO}$, which, after removal of iodosopseudocumene with chloroform, remains as a jelly, and on drying forms a pale yellow, amorphous powder. It is soluble to some extent in acetic acid, but could not be obtained crystalline. When heated, it changes colour at 120 — 125° , chemical change probably taking place, and the product on further heating decomposes completely at 171 — 175° .

Iodoxypseudocumene, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{IO}_2$, is best prepared by boiling the crude iodoso-compound with water, and, on boiling off the latter, separates in plastic white needles, which decompose with explosion at 212° ; it is only sparingly soluble in chloroform and alcohol, and insoluble in the other common solvents.
H. G. C.

Syntheses with Sodium and Nitriles. By R. WALTHER (*J. pr. Chem.* [2], 50, 91—92).—The author has attempted to substitute another compound which shows a tendency to undergo condensation, for the third molecule of the nitrile, in Meyer's method for effecting the condensation of nitriles by means of sodium (*Abstr.*, 1889, 114). By the use of ethylic formate and acetate with benzonitrile, oily products have been obtained but not yet identified. With benzonitrile and aniline, Bernthsen's benzenylphenylamidine, melting at 114° , was obtained. Phenylhydrazine (1 mol.), benzonitrile (2 mols.), and sodium (2 mols.) yielded a compound, $\text{C}_{13}\text{H}_{10}\text{N}_2$, melting at 102° ; this is still under examination.
A. G. B.

Electrolytic Reduction of Aromatic Nitro-compounds. By L. GATTERMANN (*Ber.*, 27, 1927—1941).—The reduction in strong sulphuric acid solution is brought about as previously described by the author (*Abstr.*, 1893, i, 566, and this vol., i, 72). A detailed

account of the methods employed to separate the reduction compound from the acid solution is given in the original paper.

The compound previously obtained from orthonitrotoluene is not an amidocresol, but a sulphonic acid of the same. It crystallises in colourless needles, and, when hydrolysed with hydrochloric acid, yields the amidocresol $[\text{Me} : \text{NH}_2 : \text{OH} = 1 : 2 : 5]$. This melts at 173° , and yields a dibenzoate melting at $160\text{--}161^\circ$.

The products of reduction of the following compounds have been examined:—Metanitrotoluene yields a sulphonic acid, and the sulphate of the amidocresol $[\text{Me} : \text{NH}_2 : \text{OH} = 1 : 3 : 6]$. The latter melts at 173° , and its dibenzoate at $192\text{--}193^\circ$. Nitroparaxylene yields amidoxylanol $[\text{Me} : \text{NH}_2 : \text{Me} : \text{OH} = 1 : 2 : 4 : 5]$, which crystallises in pale yellow needles, melts and decomposes at 238° , and, when treated with ferric chloride, is quantitatively converted into paraxyloquinone (m. p. 124°).

Metabromonitrobenzene yields bromamidophenol $[\text{NH}_2 : \text{Br} : \text{OH} = 1 : 3 : 4]$, which crystallises in colourless needles, melts and decomposes at 163° , and yields a dibenzoate melting at 192° . Bromonitrotoluene $[\text{Me} : \text{NO}_2 : \text{Br} = 1 : 2 : 4]$ yields the *bromamidocresol* $[\text{Me} : \text{NH}_2 : \text{Br} : \text{OH} = 1 : 2 : 4 : 5]$, which crystallises in colourless needles, melts at 215° , is converted into a bromotoluquinone melting at 106° by oxidation with ferric chloride, and yields a *dibenzoate* melting at 229° . Bromonitrotoluene $[\text{Me} : \text{NO}_2 : \text{Br} = 1 : 3 : 4]$ yields the *bromamidocresol* $[\text{Me} : \text{NH}_2 : \text{Br} : \text{OH} = 1 : 3 : 4 : 6]$. This crystallises in colourless needles, melts at 180° , and yields the same bromotoluquinone as the preceding bromamidocresol. The *dibenzoate* crystallises in colourless needles and melts at 200° .

Methylic metanitrobenzoate yields *methylic amidosalicylate*

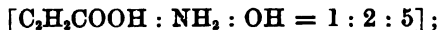


This crystallises in thick needles, melts at 96° , and gives a violet-red coloration with ferric chloride. Methylic metanitroparatoluene yields the *methylic amidocresotate* $[\text{COOMe} : \text{OH} : \text{Me} : \text{NH}_2 = 1 : 2 : 4 : 5]$, which crystallises in long, lustrous needles, and melts at 92° . The ethylic salts of the preceding acids yield similar reduction compounds. *Ethylic amidocresotate* crystallises in colourless needles and melts at $71\text{--}72^\circ$. Methylic nitrocuminate yields the *compound*



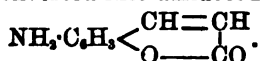
$[\text{COOMe} : \text{OH} : \text{Pr} : \text{NH}_2 = 1 : 2 : 4 : 5]$, which crystallises in bright yellow, lustrous needles and melts at $75\text{--}76^\circ$. The corresponding *ethylic salt* crystallises in colourless leaflets and melts at 61° .

Orthonitrocinnamic acid yields *amidohydroxycinnamic acid*



this crystallises from water with $1\text{H}_2\text{O}$ in broad, yellowish needles, is decomposed when heated, and when heated with concentrated hydrochloric acid at 160° is converted into hydroxycarbostyryl. The *methylic salt* prepared from methylic nitrocinnamate crystallises in beautiful golden yellow needles, and melts at $178\text{--}179^\circ$.

Metanitrocinnamic acid yields an amidohydroxycinnamic acid which is immediately converted into amidocoumarin,



This crystallises in long bright yellow needles and melts at 168°. The *acetyl-derivative* melts at 216—217°. The *benzoyl-derivative* crystallises in colourless needles and melts at 173. Ethylic metanitrocinnamate yields the same reduction product as the free acid.

The following hydroxysulphonic acids were obtained by electrolytic reduction:—Amidohydroxybenzenesulphonic acid [$\text{NH}_2 : \text{SO}_3\text{H} : \text{OH} = 1 : 3 : 4$] separates in silvery crystals, and yields paramidophenol on hydrolysis. Amidocresolsulphonic acid [$\text{Me} : \text{NH}_2 : \text{SO}_3\text{H} : \text{OH} = 1 : 2 : 4 : 5$] crystallises in broad, lustrous needles, decomposes when heated, and yields orthoamidometacresol on hydrolysis.

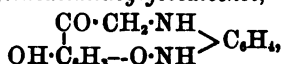
Amidohydroxyquinoline [$\text{OH} : \text{NH}_2 = 1 : 4$] is obtained by the electrolytic reduction of nitroquinoline [$\text{NO}_2 = 4$]; it melts at 143°. The *dibenzoyl-compound* crystallises in colourless plates, and melts at 205°. The *diacetyl-compound* crystallises in pale yellow needles, and melts at 206—207°. The *sulphate* crystallises in long needles, and, when treated with benzaldehyde, yields the *benzylidene-derivative* $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CHPh}$, which crystallises from alcohol, and decomposes on heating.

Amidohydroxyquinoline [$\text{OH} : \text{NH}_2 = 4 : 1$], obtained in a similar way to the preceding, separates in colourless crystals which turn green on exposure to air; it decomposes when heated, and quickly oxidises in alkaline solution, forming a bluish-green precipitate. The *diacetyl-compound* crystallises in colourless needles, and melts at 153—154°. The *dibenzoyl-compound* crystallises in thick prisms, and melts at 180°.

Amidohydroxymethylquinoline [$\text{NH}_2 : \text{Me} : \text{OH} = 4 : 3 : 1$], obtained from nitromethylquinoline [$\text{NO}_2 : \text{Me} = 4 : 3$], crystallises in long, brownish-yellow needles, and melts at 123°. E. C. R.

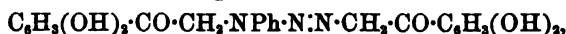
Ethereal Salts and Ketones from Phenols and Halogen Substituted Fatty Acids. By S. DZIERZGOWSKI (*Ber.*, 27, 1983—1989).

—The author has recently prepared a number of condensation products by the interaction of phenols with halogen substituted acids in presence of phosphorus oxychloride. Catechol and chloracetic acid, bromacetic acid, α -chloropropionic acid, α -bromopropionic acid, and α -bromobutyric acid yield haloïd ketones; phenol, quinol, and guaiacol, under the same conditions, yield ethereal salts; whilst resorcinol and chloracetic acid combine to form a yellowish-red dye with a green fluorescence. A number of crystalline products are also formed from chloracetypyrogallol (this vol., i, 518) and ammonia, methylamine, dimethylamine, aniline, methylaniline, dimethylaniline, paramidomethoxybenzene, quinoline, pyridine, and piperidine respectively. Of the phenylenediamines, only the ortho-derivative reacts with chloracetocatechol and chloracetypyrogallol, forming, with the former, *anhydrophenylenediimidoglycococatechol*,



crystallising in yellow needles; it decomposes at about 245° without melting, is only sparingly soluble in alkalis, but readily in concentrated sulphuric acid, being precipitated in red needles on dilution. The *acetyl-derivative* crystallises in colourless needles, melts at 141° , and gives no coloration with ferric chloride. *Anhydrophenylene-diimidoglycopyrogallol* is prepared in a similar manner to the catechol derivative which it closely resembles; it decomposes at 290° without melting, and gives a green coloration with ferric chloride. The *diacetyl-derivative* crystallises in colourless needles, and melts at 143° .

Aniline and chloracetocatechol combine to form an *anilide*, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot NHPh$. The *sulphate* crystallises in colourless needles melting at 208° ; when treated with nitrous acid, phenol is eliminated, and *catecholglycophenyltriazine*,

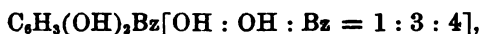


is formed; this crystallises in slender, yellow needles, melts and decomposes at 115° , is extremely unstable, and is decomposed by alkalis and by acids. *Catecholglycotolyltriazine* is prepared in a similar manner to the phenyl derivative which it closely resembles, it crystallises in prismatic needles, melts and decomposes at 120° , and is tolerably stable towards acids and alkalis. Attempts to reduce this compound were unsuccessful.

Catecholglycothiocyanate, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot S \cdot CN$, is prepared by the action of potassium or ammonium thiocyanate on chloracetocatechol, and crystallises from water in colourless prisms, melting at $147-150^{\circ}$; it gives a dark green coloration with ferric chloride, and yields a metallic mirror with alkaline silver solutions. *Pyrogallolglycothiocyanate*, formed in a similar manner to the preceding compound, crystallises in colourless needles melting at 196° .

The action of amines on ethereal chloracetates takes place in two stages, the amine radicle displaces the chlorine group, and the resulting compound is then hydrolysed by the remaining base; thus phenylic chloracetate and quinol chloracetate both yield phenylglycocineanilide by the action of aniline. Dimethoxyacetocatechol, $C_6H_5Ac(OMe)_2$, has also been prepared, and proves to be identical with Nietzel's "acetoveratrone" (Abstr., 1892, 61); acetopyrocatechol obtained by the reduction of chloracetocatechol with tin and hydrochloric acid is therefore identical with Nietzel's "acetocatechone," $C_6H_5Ac(OH)_2$; it melts at 116° , not at $96-98^{\circ}$ as stated (*loc. cit.*).
J. B. T.

Benzoresorcinol. By A. KOMAROWSKY and S. v. KOSTANECKI (*Ber.*, 27, 1997-2000).—Dihydroxybenzophenone,



is prepared by the action of benzoic trichloride on resorcinol in aqueous solution, or by heating resorcinol with benzoic acid and zinc chloride at 160° . Its constitution is established both by its analogy to resacetophenone and by the production of β -phenylumbelliferone, the *acetyl-derivative* of which crystallises in silky, lustrous needles

melting at 123° . *Trihydroxybenzophenone* [$\text{OH} : \text{OH} : \text{Bz} = 1 : 3 : 4$; $\text{CO} : \text{OH} = 1 : 4$], obtained from resorcinol, parahydroxybenzoic acid, and zinc chloride, crystallises with $2\text{H}_2\text{O}$ in yellow needles, and melts at $200-201^{\circ}$. *Dihydroxymethoxybenzophenone* [$\text{OH} : \text{OH} : \text{Bz} = 1 : 3 : 4$; $\text{CO} : \text{OMe} = 1 : 4$] is formed from resorcinol and paramethoxybenzoic acid, and crystallises in needles melting at 165° . *Tetrahydroxybenzophenone* [$\text{OH} : \text{OH} : \text{Bz} = 1 : 3 : 4$; $\text{CO} : \text{OH} : \text{OH} = 1 : 3 : 4$], obtained from resorcinol and 3 : 4-dihydroxybenzoic acid, crystallises with $2\text{H}_2\text{O}$ in almost colourless needles, melts at $201-202^{\circ}$, and dyes mordanted cloth; the colours produced resemble those given by maclurin, but are feebler.

J. B. T.

Triethylphloroglucinol. By A. COMBES (*Compt. rend.*, 118, 1336—1339).—The author has previously shown that the action of anhydrous aluminium chloride on butyric chloride yields a solid compound, $\text{C}_{12}\text{H}_{18}\text{O}_3$, which, although it contains no hydroxyl group, behaves as a monobasic acid, and forms salts which are neutral to litmus and phenolphthaleïn.

If the aluminium chloride and butyric chloride are mixed with a large quantity of chloroform instead of being allowed to act directly on one another, only 2 mols. of the acid chloride condense instead of three, and when the product is treated with water, carbonic anhydride is given off, and dipropyl ketone is formed. It follows that the first stage in the condensation is the production of the compound $\text{CH}_3\text{Me}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{COCl})\cdot\text{CH}_2\text{Me}$, which is subsequently attacked by the third molecule of butyric chloride with formation of the compound $\text{C}_{12}\text{H}_{18}\text{O}_3$. If the latter is heated with excess of dilute potassium hydroxide solution in sealed tubes at $150-160^{\circ}$ for two hours, it splits up quantitatively into dipropyl ketone, carbonic anhydride, and normal butyric acid. When heated on a water bath with phenyl hydrazine, it combines with 3 mols. of that compound.

This compound, $\text{C}_{12}\text{H}_{18}\text{O}_3$, is therefore analogous to phloroglucinol, which, according to Baeyer's researches, must be regarded as a hexamethylene derivative. The author finds that when phloroglucinol is heated with excess of dilute potassium hydroxide solution in sealed tubes at 160° , it splits up quantitatively into acetone, acetic acid, and carbonic anhydride. It follows that the compound $\text{C}_{12}\text{H}_{18}\text{O}_3$ is triethylphloroglucinol.

C. H. B.

Condensation of Dichloroacetal with Anisoil and Phenetoil. By H. WIECHELL (*Annalen*, 279, 337—344; compare this vol., i, 502, 520).—*Dianisylchloroethane*, $\text{CHCl}_2\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, crystallises in stellate groups of prisms, melting at 113° . *Dianisylchloroethylene*, $\text{CHCl}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, separates from alcohol in lamellæ, which have a bluish iridescence; it melts at 76° . *Paradimethoxytolane*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}:\text{C}:\text{C}_6\text{H}_4\cdot\text{OMe}$, forms colourless plates melting at 142° , and sparingly soluble in ether. The dibromide is a sparingly soluble substance, and crystallises from acetic acid in long, slender needles melting at 197° , whilst the tetrachloride crystallises in cubes,

and melts at 169°. Dimethoxytolane is converted by heating with acetic and sulphuric acids into deoxyanisoïn, which melts at 108—109° (stated by Rossel, *Annalen*, 151, 40, 42, as 95°). The *oxime* of this ketone crystallises in prisms melting at 125°. *Anisilmonoxime*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, prepared from deoxyanisoïn by Claisen's method (*Ber.*, 22, 379), forms colourless, slender needles melting at 130°.

Dianisylhydroxyethane, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is obtained by the reduction of deoxyanisoïn, and crystallises from alcohol in slender needles melting at 170°. *Paradiethoxystilbene*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is prepared by treating dianisylhydroxyethane with acetic and hydrochloric acids. The *dibromide* crystallises from carbon bisulphide in slender needles, melting at 145°.

Diphenetyldichlorethane, $\text{CHCl}_2\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OEt})_2$, crystallises in concentrically grouped needles melting at 72°. *Diphenetylchloroethylene* crystallises in lustrous plates, and melts at 67°. *Paradiethoxytolane* separates from acetic acid in long, highly refractive needles melting at 162°. The *dibromide* forms flat needles melting at 210°, whilst the *tetrachloride* melts at 172. *Deoxyphenetoin*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, crystallises from alcohol in plates, and melts at 102°. The *oxime* separates from benzene in needles melting at 119°. *Phenetilmonoxime* crystallises from alcohol in small needles melting at 136°. *Diphenetylhydroxyethane* forms slender, white needles melting at 147°. *Paradiethoxystilbene* crystallises in slender needles, and melts at 207°, whilst the *dibromide* forms needles melting at 192°.

A. H.

Compound of Picric acid with Anethoïl. By G. AMPOLA (*Gazzetta*, 24, i, 432—433).—Picric acid and anethoïl combine in alcoholic solution to form an *additive compound*,



it crystallises in magnificent red needles, melts at 60°, and resembles the picrates of the naphthalene hydrocarbons in properties.

W. J. P.

Official Creosote from Beech and Oak. By A. BÉHAL and E. CHOAY (*Compt. rend.*, 118, 1339—1342).—The authors apply the term "official creosote" to the constituents of creosote which boil between 200—220°. The creosote from beech has the same qualitative composition as that from oak. The monophenols are separated from the dimethyl derivatives of the diphenols after demethylating the latter by heating them with concentrated hydrochloric acid at 180°, or by passing a current of hydrogen bromide into the creosote heated at 100° in presence of a small quantity of water. The monophenols are then removed by distilling in a current of steam, and are separated by fractionation, and subsequent conversion into benzoates.

The methyl derivatives of the diphenols are separated by precipitation with strontium hydroxide, the precipitate being decomposed by hydrochloric acid. They are then fractionated, and, if necessary,

converted into carbonates by means of carbon oxychloride, and further separated by fractional crystallisation.

The official creosotes of beech and oak were thus found to contain phenol, orthocresol, metacresol, paracresol, orthoethylphenol, metaxyleneol [1 : 3 : 4], and metaxyleneol [1 : 3 : 5], guaiacol, creosol, and ethylguaiacol. They also contain small quantities of sulphur derivatives, probably thiophenol, and a compound differing from pittacal; the latter, under the influence of ammonia and air, yields a substance which dissolves in alkalis with production of a very intense blue coloration, which is turned red by acids. C. H. B.

Aniline and Toluidine Hydrogen Sulphates. By E. HITZEL (*Compt. rend.*, 118, 1335—1336).—Aniline and toluidine hydrogen sulphates are easily obtained by floating a warm saturated solution of the normal sulphate on a layer of concentrated sulphuric acid contained in a broad vessel. The liquid should then be cooled at 0°, or below, and after from 12 to 24 hours the upper layer of liquid becomes filled with crystals of the hydrogen sulphate. These should be at once removed, or they will gradually redissolve.

Aniline hydrogen sulphate, $\text{NH}_2\text{Ph}\cdot\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$, forms white lamellæ, which become slightly rose-coloured when exposed to air. *Orthotoluidine hydrogen sulphate* crystallises with $1\text{H}_2\text{O}$ in large, rhomboidal lamellæ. *Paratoluidine hydrogen sulphate* crystallises with $1\text{H}_2\text{O}$ in large needles, which become slightly rose-coloured when exposed to air. C. H. B.

Action of Primary Amines of the Benzene Series on Unsymmetrical Ketonic Compounds. By L. SIMON (*Compt. rend.*, 118, 1342—1345).—When aniline acts on pyruvic acid in presence of ether, three compounds are obtained in very unequal proportions: (1) *anilpyruvic acid*, $\text{NPh}\cdot\text{CMe}\cdot\text{COOH}$, which melts and decomposes at 126°, is profoundly altered by cold water or alcohol, is insoluble in chloroform or ether, and only slightly soluble in warm ethylic acetate or benzene. It dissolves in concentrated sulphuric acid, the solution having a beautiful, wine-red colour, which disappears on the addition of water, and changes to yellow on heating, or after standing for some time. (2) *Methylquinolinecarboxylic acid* (aniluvitonic acid), $\text{C}_8\text{NH}_7\text{Me}\cdot\text{COOH}$, a compound more stable than the preceding, from which it can be obtained by the action of water, alcohol, or heat alone; it forms beautiful, yellow crystals, soluble in warm water or alcohol, but insoluble in boiling chloroform. It melts at 246°, undergoing decomposition into carbonic anhydride and methylquinoline. Concentrated sulphuric acid dissolves it, forming a yellow solution, which retains its colour even on dilution. (3) A compound which seems to have the composition $\text{C}_{13}\text{H}_{13}\text{NO}_2$. It is very stable, melts at about 188° without decomposition, and solidifies in acicular crystals, which act on polarised light; it is insoluble in cold water or benzene, slightly soluble in ether or acetic acid, very soluble in hot chloroform, from which it separates almost completely on cooling; it also dissolves in sulphuric acid, but separates again unchanged on dilution. It is not affected by boiling aqueous solutions of potassium hydroxide.

When an alkylic salt of pyruvic acid is acted on by an amine, compounds are formed of the general composition $C_6H_5O(NPh)_2COOR$. They crystallise well, melt without undergoing decomposition, dissolve in ether, chloroform, and benzene, and also in concentrated sulphuric acid, from which they are separated unchanged on adding water.

The action of aniline on phenylglyoxylic acid in presence of ether yields white crystals of aniline phenylglyoxylate. No formation of an anilic acid takes place at the ordinary temperature, but there is some evidence that this change occurs at about 90° . If the aniline phenylglyoxylate is heated at 300° , it yields a compound which melts at 52° , dissolves in ether and alcohol, and seems to be a phenanthridine.

These experiments show that in the formation, at ordinary temperatures, of anilic derivatives of the form $NPh.CRR'$, there are no indications of isomeric modifications similar to those observed in the oximes and some of the hydrazones.

C. H. B.

Interaction of Quinones with Metanitrilaniline and Nitro-paratoluidine. By J. LEICESTER (*Chem. News*, 69, 291; compare Abstr., 1890, 1445).—*Quinonedimetanitranilide*, prepared by heating quinone and metanitrilaniline dissolved in glacial acetic acid, crystallises from a mixture of methylic alcohol and benzene, and melts at 295° . *Quinonemetanitrilide* is obtained along with the above as a bronze-coloured powder, melting at 135° .

Quinonemetahomofluorindine, $C_6H_4 \langle \begin{smallmatrix} NH \\ N \end{smallmatrix} \rangle C_6O_2 \langle \begin{smallmatrix} N- \\ NH \end{smallmatrix} \rangle C_6H_4$, formed by the reduction of the dianilide with ammonium sulphide, is a brownish-black powder, melting above 360° ; it gives a brown coloration with acetic acid, which changes to slaty green, and finally to mauve, on adding sulphuric acid gradually.

Quinoneparanitrotoluidide, obtained in a similar manner, is a bluish-black, crystalline powder; on reduction with ammonium sulphide, it yields a slate-coloured compound, which decomposes at 300° .

Quinonediparatoluidide is bronze-coloured, and yields, on reduction, a substance melting at 320° , and dissolving in alcohol, benzene, and acetic acid, with a dark greenish-yellow colour and green fluorescence.

Thymoquinonediorthonitrilide, from thymoquinone and orthonitrilaniline, crystallises from alcohol and ether in straw-coloured needles, and melts at 125° . The phenazine, $C_6O_2MePr \langle \begin{smallmatrix} N \\ N \end{smallmatrix} \rangle C_6H_4$, $[O : N : Me : O : N : C_6H_7 = 1 : 2 : 3 : 4 : 5 : 6]$, from it forms grey needles, melting at about 320° .

Thymoquinonediparanitrotoluidide crystallises from absolute alcohol in yellowish-red plates, melting at 112° ; it also forms needles.

Thymoquinoneorthomethylphenazine, $C_6O_2MePr \langle \begin{smallmatrix} N \\ N \end{smallmatrix} \rangle C_6H_4Me$, is a greyish-white, crystalline powder, subliming at 325° , and dissolving in acetic acid and ether with a yellow colour.

A number of crystalline compounds have also been obtained by the

reduction of anilides and toluidides with magnesium; the products are of a complex nature, and are being investigated. D. A. L.

Constitution of the Aniline Derivative of Glucose. By L. MARCHLEWSKI (*J. pr. Chem.* [2], 50, 95—96).—A criticism of the formula assigned to this compound by v. Miller and Plöchl (*Abstr.*, this vol., i, 413); it is claimed that Sorokin's formula (*Abstr.*, *J. pr. Chem.* [2], 37, 304) will equally well serve to explain the behaviour of the compound with hydrogen cyanide (compare *Trans.*, 1893, 1137).

A. G. B.

Orthohydroxydiphenylamine. By A. DENINGER (*J. pr. Chem.*, [2], 50, 89—90).—*Orthohydroxydiphenylamine*, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$, is prepared by heating aniline (50 grams) with catechol (59 grams), calcium chloride (25 grams), and a little carbonic acid in an autoclave at 180° for 24 hours. The product is extracted with hydrochloric acid, and the *hydrochloride* recrystallised. The base crystallises in colourless prisms, melts at 68° , and dissolves freely in ether, glacial acetic acid, and alcohol, but only sparingly in benzene or boiling water. It reduces hot Fehling's solution, and its salts give a deep blue-black coloration with ferric chloride. A *dibenzoyl*-derivative was prepared.

A. G. B.

Reaction between *n*-Aldoxime Ether and Phenyllic Thio-carbimide. By E. BECKMANN (*Ber.*, 27, 1957—1959).—The author has stated that the reaction between *n*-benzylbenzaldoxime and phenylthiocarbimide takes place according to the equation



since, by the action of sodium ethoxide, the preceding additive compound is converted into the amidine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CPh}\cdot\text{NPh}$. A further examination of the reaction with *n*-aldoxime ethers containing substituents in the aldehyde- or benzyl-groups shows that the nitrogen of the phenylic isocyanate combines with the carbon atom of

the aldehyde group to form compounds of the type $\begin{array}{c} \text{CHPh}\cdot\text{N}\cdot\text{CH}_2\text{Ph} \\ | \\ \text{NPh}\cdot\text{CO} > \text{O} \end{array}$, which, when treated with sodium ethoxide, yield amidines of the type $\text{X}\cdot\text{C}(\text{NH}\cdot\text{CH}_2\cdot\text{Y})\cdot\text{NPh}$.

The following compounds have been examined: *n*-benzylanisaldoxime, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$, m. p. 128° ; *n*-anisylbenzaldoxime,

$\begin{array}{c} \text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$, m. p. 125° ; *n*-benzylcuminaldoxime, m. p. 156° ; and *n*-cumylbenzaldoxime, m. p. 139° .

E. C. R.

The Diazotising Process. By E. BAMBERGER (*Ber.*, 27, 1948—1953).—The author has already shown that benzenediazoic acid is

easily obtained by the action of nitric anhydride on aniline (this vol., i, 239), and the nitro-group in the side chain readily "wanders" to the nucleus. The author now shows that nitrous acid acts in the same way on primary aromatic bases, whereby nitrosamines are first formed which easily undergo isomeric change and are converted into diazo-compounds. The following aromatic bases have been examined: aniline, paratoluidine, α -naphthylamine, β -naphthylamine, ortho-, meta-, and para-nitraniline, parabromaniline, metanitroparatoluidine, paranitroorthotoluidine, orthonitroparatoluidine, metanitroorthotoluidine, and 1:4-nitronaphthylamine. In all cases, diazo-compounds are obtained, together with the isodiazo-compounds, as the former so readily undergo molecular change. The isodiazo-compounds are more stable according as the nature of the base is more negative. Metanitraniline and α -naphthylamine are, however, exceptions to this rule. It is important that only small quantities of the base should be employed for each experiment, as, otherwise, the prolonged duration of the action is sufficient to convert the iso-compound into the diazo-compound. Thus, with 15 grams of paranitraniline, no nitroisodiazo-benzene was obtained, whereas with 5 grams it was easily obtained.

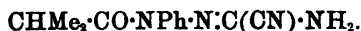
From these results, the author concludes that nitrous acid acts in the same way both on primary and secondary bases, namely, to form nitrosamines, and that the difference between the two classes of aromatic bases is the result of a secondary action.

The experiments are carried out as given below for paranitraniline. A dry solution of nitrous anhydride is gradually added to paranitraniline dissolved in a mixture of equal volumes of ethylic acetate and ether at a temperature of -5° . The crystalline precipitate obtained contains diazoparanitraniline, paranitraniline, and diparadinitrodiazamidobenzene (m. p. 233°). The ethereal filtrate is shaken with ice-cold water, to extract the remaining diazoparanitraniline, and then the isoparanitrodiazobenzene is extracted with very dilute ammonia.

E. C. R.

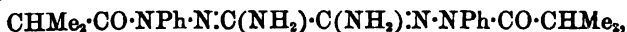
Action of Cyanogen on α -Acidylphenylhydrazides. By O. WIDMAN (*Ber.*, **27**, 1962—1968).— α -Isobutyrylphenylhydrazide, which previously has been described as an oil, can be obtained crystalline if α -isobutyryl- β -acetylphenylhydrazide, prepared by the action of isobutyric chloride on acetylphenylhydrazide, is boiled with dilute sulphuric acid and alcohol, and the product extracted with ether. It crystallises in colourless tablets or broad needles, and melts at $46-48^{\circ}$.

β -Dicyan- α -isobutyrylphenylhydrazine,



is obtained by saturating an aqueous solution of the preceding compound with cyanogen and allowing it to remain in a closed flask for two days. It melts at 150° , crystallises in beautiful, colourless leaflets or tablets, and is very easily decomposed with the formation of a triazole-compound.

β -Cyanodi- α -isobutyrylphenylhydrazine,



is obtained together with the preceding compound, and may be isolated by taking advantage of its being less soluble. It crystallises in small, short needles or prisms, and melts at 217° .

Cyanisopropylphenyltriazole, $\text{NPh} < \begin{smallmatrix} \text{C}(\text{CHMe}_2):\text{N} \\ \text{N}=\text{C} \cdot \text{CN} \end{smallmatrix}$, is obtained from the above dicyanisobutyrylphenylhydrazine by evaporating its alcoholic solution with a few drops of hydrochloric acid or by allowing the aqueous solution to remain exposed to the air for some time. It crystallises in colourless, six-sided tablets, or large, thin plates, and melts at $76-77^{\circ}$. When warmed with dilute potassium hydroxide, it yields *isopropylphenyltriazolecarboxylic acid*; this crystallises in plates containing benzene, which melt at 112° , whilst the dry substance melts at 153° with evolution of gas. The *amide* crystallises in small, colourless pyramids, and melts at $144-146^{\circ}$.

Bladin (Abstr., 1892, 637) has prepared a cyanisopropylphenyltriazole by heating dicyanphenylhydrazine with isobutyric anhydride; it yields a carboxylic acid, melting at 135° , and an amide, melting at $127.5-128^{\circ}$. The author has repeated Bladin's experiments and finds that he was working with impure materials. The author obtained the above triazole by the action of isobutyric anhydride on dicyanphenylhydrazine.

β -Isobutyrylphenylhydrazide is obtained by the action of isobutyric chloride on phenylhydrazine. It crystallises in rhombic tablets and melts at 140° . E. C. R.

Diacid Anilides. By G. TASSINARI (*Gazzetta*, 24, i, 444-449; compare this vol., i, 285).—On heating diacetanilide with acetic acid, it is partially converted into acetanilide, acetic anhydride being formed.

Parachlorodiacetanilide, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N} \cdot \text{Ac}_2$, is prepared by heating parachloracetanilide with acetic anhydride and anhydrous sodium acetate; it is soluble in benzene, alcohol, or ether, and separates in large crystals melting at $66-67^{\circ}$. One acetyl-group is eliminated on treating it with N/10 soda at 70° .

Metanitrodiaacetanilide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{Ac}_2$, is formed on heating metanitroacetanilide with acetic anhydride and sodium acetate; it is very soluble in benzene or ether, and is obtained in large, colourless crystals melting at $76-77^{\circ}$. On heating with N/10 soda, it is converted into metanitroacetanilide; this forms small, colourless crystals melting at $152-153^{\circ}$, not yellow crystals melting at $140-141^{\circ}$, as stated by Meyer and Stüber (*Annalen*, 165, 173).

Monacetyloxanilide, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2$, is prepared by heating oxanilide with acetic anhydride and sodium acetate in a reflux apparatus; it is a crystalline powder melting at about $197-198^{\circ}$. When heated with N/10 soda, it is converted into diphenylethenylamidine.

Ethenylparaditolylamidine, $\text{C}_{16}\text{H}_{18}\text{N}_2$, is obtained by heating paraoxatoluidide with N/10 soda; it crystallises in colourless needles and melts at $120-121^{\circ}$. W. J. P.

Study of the Mono- and Bi-basic Hydroxy-acids. By C. A. BISCHOFF (*Annalen*, 279, 153-188).—In this paper, the author sum-
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marises and discusses the results described in papers by Walden and himself (the two following abstracts, and this vol., i, 493, 495, 496, 525) in accordance with his "dynamical hypothesis" (Abstr., 1891, 892).

On heating potassium chloromalonate, potassium chloride is formed and carbonic anhydride evolved; no other product could be isolated. *Potassium chloromethylmalonate* is a colourless, crystalline salt which behaves similarly to the preceding when heated; if it is heated in heavy petroleum, small quantities of acrylic acid (?) are formed.

Propionylparatoluidide, $C_6H_4Me \cdot NH \cdot CO \cdot CH_2Me$, crystallises in colourless tablets melting at 126° . *Isobutyrylorthotoluidide* is obtained in colourless needles melting at $115-116^\circ$ and is identical with a substance prepared by Tigerstedt (Abstr., 1893, i, 51). *Isobutyrylparatoluidide* crystallises in colourless leaflets melting at 109° . *Phenylacetylorthotoluidide*, $C_6H_4Me \cdot NH \cdot CO \cdot CH_2Ph$, is obtained in colourless needles melting at 159° .

Ladenburg's formylorthotoluidide (*Ber.*, 10, 1128) is really oxalorthotoluidide: when heated with phosphorus pentachloride, it yields *oxalotoluidimidochloride*, $C_6H_4Me \cdot N : CCl \cdot CCl : N \cdot C_6H_4Me$, in long, yellow needles melting at $130-131^\circ$.

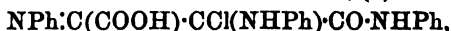
W. J. P.

Derivatives of Malic Acid. By C. A. BISCHOFF and P. WALDEN (*Annalen*, 279, 130-137; compare Bischoff, Abstr., 1891, 1220).—Anilidosuccinanil and dichlormaleindianil (compare Bearis, *Inaug. Diss.*, Bonn, 1892) are formed on treating malic dianilide with phosphorus pentachloride. The succinanil is also obtained by heating maleic acid with aniline and water; it is then accompanied by *aniline maleate*, $C_2H_2(COOH)_2(NH_2Ph)_2$, a crystalline substance melting at $143-144^\circ$ (compare Osipoff, Abstr., 1889, 124).

The fumaric diparatoluidide already described by Bischoff (Abstr., 1891, 1220) and Giustiniani's paratolylfumaramide (Abstr., 1893, i, 264), are, in all probability, maleic diparatoluidide. Phosphorus pentachloride, in absence of a diluent, acts on malic diparatoluidide with formation of paratoluidine hydrochloride and *chlorosuccinyltolyl*, $CHCl \cdot CO$
 $CH_2 \cdot CO > N \cdot C_6H_4Me$, which crystallises in slender needles melting at $156-158^\circ$. On treating malic diparatoluidide, suspended in benzene, with phosphorus pentachloride, *chlorosuccinic diparatoluidide*, $C_6H_4Me \cdot NH \cdot CO \cdot CH_2 \cdot CHCl \cdot CO \cdot NH \cdot C_6H_4Me$, is obtained. It decomposes without melting at above 250° , and is accompanied by other substances which could not be purified.

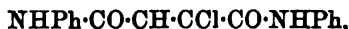
W. J. P.

Derivatives of Tartaric Acid. By C. A. BISCHOFF and P. WALDEN (*Annalen*, 279, 138-152).—Tartranilide melts at $263-264^\circ$, whilst diacetyltartranilide melts at $214-215^\circ$; the melting points given by Polikin (Abstr., 1892, 54) are erroneous. On treating tartranilide, suspended in benzene, with phosphorus pentachloride, dichlormaleindianil and *anilanolidochlorosuccinic monanilide*, (?)



are formed; the latter melts at $170-178^\circ$, and was not obtained pure. The supposed piperazine derivative, described by Bischoff and others

(Abstr., 1893, i, 54, 564), is also formed in this reaction; numerous unsuccessful attempts were made to prepare this compound from dianilidosuccinic acid, and so throw light on its constitution, which is still problematic. *Chlorofumaric dianilide*,



is not formed when phosphorus pentachloride acts on tartranilide, but it is readily produced by the interaction of chlorofumaric chloride and aniline; it crystallises in colourless needles melting at 186° .

The four substances next described are formed on treating tartaric paratoluidide with phosphorus pentachloride.

1. *Toluidochloromaleintolyl*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \overset{\text{Cl} \cdot \text{CO}}{\underset{\text{CO}}{\text{C}}} > \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$, crystallises in yellow prisms melting at $198-199^\circ$; this substance may equally well be the tautomeric tolylchlorosuccintolyl.

2. A *trichloro-derivative*,



is obtained in white needles melting at $192-192.5^\circ$.

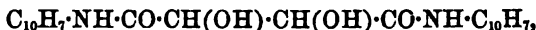
3. *Tolyltoluidochlorosuccinic monotoluidide*,



crystallises in yellow needles melting at 186° .

4. A substance of the composition $\text{C}_{25}\text{H}_{21}\text{N}_3\text{ClPO}_7$, which forms an amorphous, colourless powder melting at $220-221^\circ$; it is readily decomposed by dilute soda.

Tartaric di- α -naphthalide,



prepared by heating tartaric acid with α -naphthylamine at 180° , crystallises in colourless needles melting at 214° . It readily yields a *diacetyl-derivative* which forms colourless needles melting at 260° . On heating the naphthalide with benzoic chloride, the *dibenzoyl-derivative* is obtained; it melts at $215-217^\circ$ with decomposition, and is accompanied by benzoyl- α -naphthalide.

Tartaric di- β -naphthalide crystallises in silvery leaflets melting at 280° . Its *diacetyl-derivative* is obtained in colourless needles melting at 240° , whilst the *dibenzoyl-derivative* forms white, nodular crystals melting at $179-180^\circ$; the latter substance is accompanied by benzoyl- β -naphthalide.

W. J. P.

Derivatives of "Phenocoll," of Paramidophenetoil, and of Anisidine. By F. NICOLA (*Chem. Centr.*, 1894, i, 418-419; from *Ann. Chim. Farm.*, 18, 353-365).—The knowledge of "phenocoll," $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2$, and its derivatives being somewhat uncertain, the author has restudied the subject. The free base was prepared from the commercial chloride. It forms white needles soluble in alcohol and in boiling water; the crystals contain $1\text{H}_2\text{O}$, which they lose at $80-90^\circ$, and the anhydrous base then melts at 99.5° ; at a slightly higher temperature ammonia is evolved,

leaving a residue which gives a fine, reddish-violet coloration with ferric chloride. The platinochloride forms anhydrous, yellow prisms, whilst the chloride crystallises with 1 mol. aq. "*Cyanacetophenocoll*," $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$, obtained by the action of cyanacetic acid on phenocoll, yields white crystals melting at 28° . When oxidised with potassium permanganate, it yields "*phenocoll-oxamic acid*," $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{COOH}$, forming small, white crystals soluble in alcohol or water; it melts and decomposes at 202° .

Cyanacetoparamidophenetoil, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$, is obtained by the action of ethylic cyanacetate on paramidophenetoil. It crystallises in white needles melting at 180 – 181° . When oxidised with potassium permanganate, it yields *ethoxyphenyloxamic acid*,



in small, white crystals melting and decomposing at 180° .

Cyanacetoanisidine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$, forms glistening, white needles melting at 136° ; it yields *methoxyphenyloxamic acid* on oxidation.

Diethoxyphenylmalonamide, $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, and *dimethoxyphenylmalonamide* are formed as bye-products during the preparation of the two last-named cyano-derivatives.
L. T. T.

Amidoguanidine. By G. PELLIZZARI and G. CUNEO (*Gazzetta*, **24**, i, 450–467; compare Pellizzari, *Abstr.*, 1892, 579).—Amidoguanidine is readily prepared by heating an alcoholic solution of hydrazine hydrochloride with cyanamide in a reflux apparatus (compare Thiele, *Abstr.*, 1892, 1295).

Orthotolylamidoguanidine, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4$, is prepared by boiling an alcoholic solution of orthotolylhydrazine hydrochloride and cyanamide. A poor yield of the base is obtained on heating orthotolylhydrazine hydrochloride and guanidine carbonate at 150 – 160° . The *hydrochloride* crystallises in large, red prisms melting at 212° ; it is soluble in alcohol or water. The *nitrate* crystallises in colourless needles and melts at 206.5° . The *platinochloride* is obtained in beautiful, yellow needles, whilst the *picrate* crystallises in massive, yellow needles melting at 206° .

Paratolylamidoguanidine is prepared in a similar way to its ortho-isomeride. Its *hydrochloride* crystallises in transparent scales melting at 196.5° , and is very soluble in water or alcohol. The *nitrate* is obtained in colourless laminae melting at 181° , and is sparingly soluble in water. The *platinochloride* separates from its aqueous solution in red crystals, whilst the *picrate* crystallises in yellow needles melting at 212° .

α -Naphthylamidoguanidine, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, prepared from cyanamide and α -naphthylhydrazine hydrochloride, yields a *hydrochloride* which crystallises in small, colourless needles melting at 166° . The *platinochloride* is obtained as a yellow, crystalline powder.

β -Naphthylamidoguanidine hydrochloride separates from aqueous solution in minute crystals which decompose at 250 – 260° ; it is very

soluble in alcohol, sparingly so in cold water. The *nitrate* forms small crystals melting at 230° , and is sparingly soluble in water. The *platinochloride* is a red, crystalline powder, whilst the *picrate* is a yellow, crystalline powder sparingly soluble in water.

The salts of the tolyl- and naphthyl-amidoguanidines reduce ammoniacal silver nitrate, and do not react with benzaldehyde. The free bases could not be isolated, as they decompose as soon as formed.

Ethylphenylamidoguanidine, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NEtPh}$, is prepared by heating α -ethylphenylhydrazine hydrochloride with cyanamide; the *platinochloride* is obtained as a yellow, flocculent precipitate melting and decomposing at 150° . The *picrate* crystallises in red prisms melting at 224° ; it is accompanied by another *picrate* which crystallises in transparent scales melting at 269° .

Phenylamidomethylguanidine, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NMe}\cdot\text{NHPh}$, is obtained by heating hydrazomethylphenyl hydrochloride with cyanamide in alcoholic solution. The *hydrochloride* crystallises in white, transparent prisms, melts at 227° , and is very soluble in water or alcohol; the *platinochloride* is obtained in thin, red needles. The *nitrate*, which forms white crystals melting and decomposing at 105 – 106° , is very soluble in water or alcohol. The *picrate* crystallises in yellow needles melting and decomposing at 215° . W. J. P.

Guanazole and its Derivatives. By G. PELLIZZARI (*L'Orosi*, 17, 143–155, 185–192; compare *Abstr.*, 1892, 356).—*Paratolylguanazole*, $\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NH}\cdot\text{C}(\text{NH})\text{C}_6\text{H}_4$, is obtained, with evolution of ammonia, on heating paratolylhydrazine hydrochloride with dicyanodiamide in molecular proportion, at 140 – 200° ; it crystallises in yellowish prisms, melts at 172° , and is soluble in water or alcohol. It dissolves in acids, and is reprecipitated on adding potash; this fact is taken advantage of in its purification. The *hydrochloride*, $\text{C}_8\text{H}_8\text{N}_4\cdot\text{C}_6\text{H}_4\cdot\text{HCl}$, crystallises in white needles melting at 256° , and is readily soluble in water or alcohol. The *platinochloride*, $(\text{C}_8\text{H}_8\text{N}_4)_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in lustrous, yellow needles melting at 93° . The *nitrate*, $\text{C}_8\text{H}_8\text{N}_4\cdot\text{HNO}_3$, separates from water in aggregates of small needles melting at 155° . The *picrate* crystallises in transparent, yellow needles melting at 218° .

Orthotolylguanazole, $\text{C}_8\text{H}_8\text{N}_4\cdot\text{C}_6\text{H}_3$, is prepared by a process similar to that which yields its para-isomeride; it forms large, reddish crystals melting at 159° , and is soluble in water or alcohol. The *hydrochloride* separates in large, hard crystals melting at 202° . The *nitrate* crystallises in prisms melting at 226° , and is sparingly soluble in water. The *picrate* separates from its aqueous solution in small crystals melting at 212° .

β -*Naphthylguanazole*, $\text{C}_{10}\text{H}_7\text{N}_4\cdot\text{C}_{10}\text{H}_7$, crystallises in transparent laminae melting at 199° ; it is soluble in alcohol, but only sparingly so in water. The *hydrochloride* crystallises in thin, white needles melting at 255° . The *platinochloride* is obtained in very minute, yellow crystals, and is sparingly soluble in water.

Phenylmethylguanazole, $\text{C}(\text{NH})\cdot\text{NMe}\cdot\text{NH}\cdot\text{C}(\text{NH})\text{C}_6\text{H}_5$, is prepared by heating

methylphenylhydrazine hydrochloride with dicyanodiamide at 130°; it forms small, white crystals melting and decomposing at 208°, and is soluble in water or alcohol. The *hydrochloride* is very soluble in water, and crystallises in transparent prisms which do not melt at 275°; the *platinochloride* crystallises in small, yellow needles, whilst the *nitrate* forms large, yellowish crystals which, at 245°, melt and decompose.

Guanazole, $\begin{matrix} \text{C}(\text{NH})\cdot\text{NH} \\ \text{NH}\cdot\text{C}(\text{NH}) \end{matrix} > \text{NH}$, is most readily prepared by heating hydrazine monohydrochloride and dicyanodiamide with alcohol at 100°; only a small yield of guanazole is obtained on heating without alcohol. It crystallises from water in beautiful, transparent, monosymmetric crystals melting at 206°; $a : b : c = 4.2743 : 1 : 2.4967$. $\beta = 88^\circ 14'$. It is soluble in water or alcohol, but insoluble in ether, chloroform, or benzene; its aqueous solution has a feebly alkaline reaction, and, on the addition of potassium nitrite and acid, deposits a yellow *nitroso*-derivative. On crystallising a solution of guanazole in hydrochloric acid, the dihydrochloride is obtained in long needles melting at 145°; it has a strongly acid reaction, and dissociates in aqueous solution. The *monohydrochloride* is obtained by repeatedly evaporating the aqueous solution of the acid salt with water or alcohol; it crystallises in white prisms melting at 100°, and is very soluble in water or alcohol; no platinochloride could be prepared. The *sulphate*, $\text{C}_2\text{N}_4\text{H}_6\cdot\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, separates from its solution in small, white prisms which lose their water at 100°; the *nitrate*, $\text{C}_2\text{N}_4\text{H}_6\cdot\text{HNO}_3$, is obtained in very small crystals melting at 165°, and is very soluble in water; the *picrate*, $\text{C}_2\text{N}_4\text{H}_6\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, crystallises in flat needles melting at 245°. *Guanazole silver nitrate*, $\text{C}_2\text{N}_4\text{H}_6\cdot\text{AgNO}_3$, is obtained by adding silver nitrate to an aqueous solution of guanazole; it forms white flocks soluble in nitric acid or ammonia, and slowly blackens on exposure to light; *guanazole copper sulphate*, $\text{C}_2\text{N}_4\text{H}_6\cdot\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, is a green, crystalline precipitate, obtained on adding copper sulphate to a solution of guanazole; it loses its water at 200°. A *substance* of the composition $2\text{C}_2\text{N}_4\text{H}_6\cdot\text{HgCl}_2\cdot\text{HgCl}_2$, is precipitated as a white powder on adding mercuric chloride to an aqueous solution of guanazole; it is insoluble in water, but dissolves in acids. On dissolving it in warm hydrochloric acid, and cooling, a *substance* of the composition $2(\text{C}_2\text{N}_4\text{H}_6\cdot\text{HCl})\cdot\text{HgCl}_2$ separates in long, white needles; whilst if crystallised from water, nodular masses of white needles of a *substance* of the composition $\text{C}_2\text{N}_4\text{H}_6\cdot\text{HCl}\cdot\text{HgCl}_2$ separate.

W. J. P.

Synthesis of Hydroxy-aromatic Bases. By M. NENCKI (*Ber.*, 27, 1969—1979).—The condensation products of chloracetopyrogallol or chloracetocatechol and quinoline are readily decomposed by alkalis; the corresponding derivatives of isoquinoline, however, are more

stable. *Catecholglycoisoquinoline*, $\text{OH}\cdot\text{C}_6\text{H}_3 < \begin{matrix} \text{CO}\cdot\text{CH}_2 \\ \text{O}-\text{NC}_6\text{H}_7 \end{matrix} + 2\text{H}_2\text{O}$,

is prepared from the chloride (see below) by the action of alkalis or ammonia, and forms glittering, orange-coloured crystals which darken on drying; the base gives a red coloration with highly dilute ferric

chloride, whilst with excess of the latter the colour is green; both the chloride and the base dye cotton mordanted with iron, aluminium, or chromium salts, black, yellow, or reddish-brown respectively. The *chloride*, $C_8H_7(OH)_2 \cdot CO \cdot CH_2 \cdot C_6NH_7Cl + \frac{1}{2}H_2O$, is prepared from chloracetocatechol and isoquinoline, and forms colourless crystals. The *sulphate*, *tartarate*, and *oxalate* are crystalline, and are decomposed completely by the action of alkalis in excess, indicating that the base is actually an anhydride, as represented above. *Pyrogallolglycoisoquinoline* crystallises in small, rose-coloured hexagonal plates, and is decomposed by boiling with water or exposure to air. The *hydrochloride*, $C_8H_7(OH)_2 \cdot CO \cdot CH_2 \cdot C_6NH_7 \cdot HCl$, crystallises in slender, colourless needles. The *platinochloride* crystallises with 3 or 4 H_2O , according to circumstances, in small, yellow needles. *Pyrogallolglycotetrahydroquinoline*, $C_8H_7(OH)_2 \cdot CO \cdot CH_2 \cdot C_6NH_{10}$, is prepared in a similar manner to the preceding compounds, and is deposited from alcohol in yellow crystals melting at $177-178^\circ$. It forms amorphous, yellow, metallic salts, and does not combine with acids. The *sulphonic acid*, $C_{17}H_{16}NO_4 \cdot SO_3H$, crystallises in colourless plates melting at 188° . By the action of phenylhydrazine on the tetrahydroquinoline derivative, under the most varied conditions, the compound,



is formed; it crystallises in slender, yellow, silky, lustrous needles melting at $214-215^\circ$. *Catecholglycotetrahydroquinoline*, $C_{17}H_{17}NO_3$, is prepared in a similar manner to the pyrogallol derivative, and crystallises in yellow, lustrous plates melting at 170° . The *sulphonic acid*, $C_{17}H_{16}NO_3 \cdot SO_3H$, is crystalline, and gives a deep-red coloration with ferric chloride or nitric acid. Tetrahydroisoquinoline is oxidised by the action of the chloroketones which then combine with the resulting isoquinoline in the manner described above.

Vanillethylenequinoline, $OH \cdot C_6H_3(OMe) \cdot CH^4 : CH^3 \cdot C_6NH_4$, is prepared by the action of hydroxymethoxybenzaldehyde [$CH : OMe : OH = 1 : 3 : 4$] on quinaldine, and crystallises in glittering, yellow plates melting at 182° . It dissolves sparingly in acids, forming crystalline salts, is insoluble in alkali carbonates, and gives a yellowish-red coloration with ferric chloride. The *sodium salt* is yellow and crystalline. The *hydrochloride* crystallises in red needles with $2\frac{1}{2}H_2O$; the *platinochloride* is red and amorphous. The *dibromide*, $C_{18}H_{16}Br_2O_2N$, forms yellow crystals, it darkens at 220° , but does not melt, and dissolves in concentrated sulphuric acid without evolution of hydrogen bromide. On reduction, by means of sodium in alcoholic solution, the base is converted into *vanillethyltetrahydroquinoline*, $OH \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH_2 \cdot C_6NH_{10}$, which forms colourless crystals melting at 88° , and is not poisonous. The yield is good. The *hydrochloride* crystallises in pale yellow needles, and gives a characteristic red coloration with ferric chloride or dilute nitric acid. *Piperonethylenequinoline* is prepared in a similar manner from quinaldine and piperonal; it crystallises in pale yellow needles, melts at 155° , and gives no coloration with ferric chloride. The *hydrochloride* crystallises in red needles. Opianic acid and quinaldine condense,

forming *opianylquinaldine*, $C_{20}H_{17}NO_4$, which crystallises with $1H_2O$ in colourless needles, melts at 103° , becomes yellow and anhydrous at 105° , and melts again at $174-175^\circ$. It is readily soluble in dilute acids, insoluble in alkalis, but is hydrolysed by the prolonged action of soda. The compound is optically inactive, its constitution and relationship to berberine, with which it is isomeric, are being investigated. The *hydrochloride* crystallises in yellow needles. Two *platinochlorides* were obtained, the one, $(C_{20}H_{17}NO_4)_2 \cdot H_2PtCl_6$, is yellow and amorphous, the other forms hydrated crystals.

Crystalline condensation products of dihydroxybenzaldehyde [$CH:OH:OH = 1:3:4$] and furfuraldehyde with quinaldine have also been prepared. In common with piperonethylenequinoline, they are reduced to colourless, crystalline bases, when treated in alcoholic solution with sodium; the yield is almost quantitative.

J. B. T.

Refraction Constants of Coumarone and of Indene. By G. GENNARI (*Gazzetta*, 24, i, 468—474).—The author has determined the refraction constants of coumarone for the rays H_α , H_β , H_γ , and D at

16.3° . The values for the line H_α are for $P \frac{\mu_{H_\alpha}^2 - 1}{d}$, 60.6 (observed) and 60.2 (calculated); for $P \frac{\mu_{H_\alpha}^2 - 1}{(\mu_{H_\alpha}^2 + 2)d}$, 34.89 (observed) and 34.78 (calculated).

Some measurements were also made with indene; the sample used, however, contained oxygen, and the results obtained are not so trustworthy as those given by Perkin (*Trans.*, 1894, 228). W. J. P.

Benzoic Peroxide, an Oxidation Product of Benzaldehyde. By E. ERLKENYER, Jun. (*Ber.*, 27, 1959—1962).—The author has obtained benzoic peroxide from the mother liquor of the condensation products of benzaldehyde with acetic anhydride, after it had been exposed to the air for some time. Benzoic peroxide is easily obtained by allowing a mixture of benzaldehyde and acetic anhydride, mixed with sand, to remain exposed to the air for three days. The product has a strong odour of ozone, which can be easily detected by potassium iodide and starch, and yields benzoic peroxide when extracted with warm ether. Benzoic peroxide is also obtained in the same way from a mixture of benzaldehyde and benzoic anhydride.

The author was unable to obtain benzoic peroxide from benzaldehyde when acetic acid, benzene, ether, or ethylic benzoate was substituted for acetic anhydride. E. C. R.

Preparation of Diphenylacetaldehyde and Synthesis of Tolane Derivatives. By P. FRITSCH (*Annalen*, 279, 319—323; compare this vol., i, 502, 507).—Dichloroacetal condenses with hydrocarbons to form asymmetric disubstitution derivatives of dichloroethane, $CHX_2 \cdot CHCl$, which, on treatment with potash, pass into the corresponding derivatives of monochlorethylene, $CX_2 \cdot CHCl$. These again, when acted on with sodium ethoxide, react in two different ways.

Diphenylmonochlorethylene yields, as chief product, diphenylvinyl ethyl ether, $\text{CPh}_2\text{:CH}\cdot\text{OEt}$, accompanied by a small amount of tolane, CPh:CPh , whereas ditolyl-, dianisyl-, and diphenetyl-monochlorethylene do not yield substituted vinyl ethyl ethers, but are entirely converted into the corresponding para-substituted tolanes.

A. H.

Metahydroxyacetophenone. By P. BIGINELLI (*Gazzetta*, 24, i, 437—444).—*Metamidoacetophenone*, $\text{C}_6\text{H}_4\text{Ac}\cdot\text{NH}_2$, is prepared by reducing metanitroacetophenone with tin and hydrochloric acid; it crystallises in thin, yellow laminæ, and melts at $93\text{--}94^\circ$. The *hydrochloride* crystallises in micaceous laminæ, melting and decomposing at $167\text{--}168^\circ$; it is very soluble in water, and is partly converted into another hydrochloride on boiling with alcohol. No platinumchloride could be prepared.

Metahydroxyacetophenone, $\text{C}_6\text{H}_4\text{Ac}\cdot\text{OH}$, is obtained by diazotising the hydrochloride of the preceding base with potassium nitrite; the diazo-compound gradually decomposes, yielding the hydroxy-derivative, which is ultimately obtained in small needles melting at $92\text{--}93^\circ$. It has a phenolic odour, and is soluble in dilute soda, being precipitated from the solution by carbonic anhydride. It gives no colour reaction with ferric chloride. No hydrazone could be isolated.

Metahydroxyphenylmethylcarbinol, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{OH}$, is formed on reducing, with sodium amalgam, the preceding compound dissolved in methylic alcohol; it crystallises in small prisms, and melts at $116\text{--}117^\circ$.

W. J. P.

Resacetophenone. By A. WECHSLER (*Monatsh.*, 15, 239—248).—When dihydroxyacetophenone (resacetophenone) is treated with alkaline permanganate, it is only partially converted into acetic acid and a resinous substance, which has not been further examined. The greater part of the original substance is recovered unaltered. When treated with alcoholic soda on the water-bath, only a very small quantity of acetic acid is formed, and this is probably due to the oxidising action of the alkali.

Dibromodihydroxyacetophenone is obtained by adding excess of bromine to an acetic acid solution of dihydroxyacetophenone. It separates in small, lustrous crystals, melts at $173\text{--}174^\circ$, and turns red on exposure to air.

Dihydroxyacetophenoneoxime separates in pale, yellowish-green crystals, melts and decomposes at $198\text{--}200^\circ$, and, with ferric chloride, gives a coloration similar to that of dihydroxyacetophenone.

Diethoxyacetophenone, obtained in the usual way, crystallises in triclinic needles, melts at 78° , is insoluble in water, alkali hydroxides and carbonates, and gives no coloration with aqueous ferric chloride. It yields a crystalline brominated derivative, and gives a green solution with concentrated nitric acid. When heated with concentrated hydrochloric acid at 160° , it is converted into a brownish-red dye, which is insoluble in alkali carbonates, but dissolves in alkali hydroxides, yielding a beautiful bright-red solution.

E. C. R.

Action of Nitrosyl Chloride on Menthone. By A. BAAYER and O. MANASSE (*Ber.*, 27, 1912—1915).—Claisen and Manasse have shown that, under suitable conditions, camphor is readily converted by amylic nitrite into the isonitrosoketone, $\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CMe} \\ \text{CPr}^{\beta} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{OH}$, from which the corresponding camphorquinone may be prepared (*Abstr.*, 1893, i, 479). The authors have endeavoured to convert the analogous menthone into similar derivatives, but found that in this case the action proceeds in a different manner, a *tertiary nitroso-derivative*, $\text{CH}_3 \begin{smallmatrix} \text{CH}_2 - \text{CHMe} \\ \text{CPr}^{\beta}(\text{NO}) \cdot \text{CO} \end{smallmatrix} \text{CH}_3$, being obtained. It is prepared by adding amylic nitrite very slowly to a mixture of menthone and hydrochloric acid, then shaking the product with ice, and adding dilute soda; the residual oil contains undissolved nitrosomenthone, which, after recrystallisation from ether, forms lustrous needles, and melts at 112.5° , undergoing decomposition. The chief product of the action of the amylic nitrite is, however, found in the soda solution, and is an open chain acid, derived from nitrosomenthone by the addition of the elements of water; it has the constitution,



the opening of the chain taking place between the carbonyl group, and the carbon atom combined with the isopropyl group. This acid, *dimethyl-2:6-oximido-3-octanic acid*, forms crystals which melt at 98.5° , and, on boiling with dilute acids, yields the corresponding ketonic acid, which is identical with the oxymenthyllic acid described by Arth (*Abstr.*, 1886) and Mehrländer (*Inaug. Diss. Leipzig*, 1887).

H. G. C.

Removal of Hydrogen from Hydrogenised Benzenecarboxylic Acids. By A. EINHORN and R. WILLSTÄTTER (*Annalen*, 280, 88—95).—The method described consists in heating the acid for two hours at 200° with the theoretical quantity of bromine, calculated on the scale of one molecular proportion of the halogen for every two atoms of added hydrogen. Paratoluic acid is obtained almost quantitatively from Δ^1 -tetrahydroparatoluic acid (following abstract) and from hexahydroparatoluic acid (paraoctonaphthenic acid, Markovnikoff, this vol., i, 245), whilst Δ^1 -tetrahydroterephthalic acid and fumaroid hexahydroterephthalic acid yield terephthalic acid. Less satisfactory results are obtained with ortho- and meta-hexahydrotoluic acids, and it does not appear that carboxy-derivatives of other polymethylene systems behave in this way.

M. O. F.

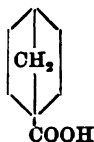
Hydrogenised Paratoluic Acids. By A. EINHORN and R. WILLSTÄTTER (*Annalen*, 280, 159—165; compare *Abstr.*, 1893, i, 713).—Hexahydroparatoluic acid (this vol., i, 245) was brominated by the method described by v. Baeyer (*Abstr.*, 1888, 1075), sufficient bromine being employed for the introduction of one atom of the halogen. α -Bromo-hexahydroparatoluic acid prepared in this way melts at $71-72^\circ$; it is scarcely soluble in water, but dissolves readily in all other ordinary solvents. Dissolved in soda, it remains unattacked by a cold solution of potassium permanganate.

Δ^1 -Tetrahydroparatoluic acid is obtained from the foregoing compound on removing hydrogen bromide by means of hot quinoline, the substance being purified by distillation in a current of steam; it forms odourless needles and plates, and melts at 132° . Potassium permanganate is immediately decolorised by its alkaline solution, although it remains unattacked when boiled with potassium ferricyanide, and has no reducing action on cupric acetate or an ammoniacal silver solution. The *amide* crystallises in flat, lustrous needles, and melts at 148° . M. O. F.

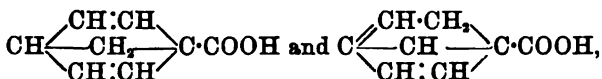
Paramethylenedihydrobenzoic acid. By A. EINHORN and R. WILLSTÄTTER (*Annalen*, 280, 96—159; compare Abstr., 1893, i, 713, and Einhorn and Tahara, Abstr., 1893, i, 378).—The reduction of this acid has yielded results which cause the authors to so far modify the view of its constitution adopted by Einhorn and Tahara

(*loc. cit.*) as to represent it by the formula $\text{C} \begin{array}{c} \text{CH}\cdot\text{CH}_2 \\ \text{CH}_2 \\ \text{CH}\cdot\text{CH} \end{array} \text{C}\cdot\text{COOH}$.

It is, therefore, $\Delta^2,4$ -paramethylenedihydrobenzoic acid, this conclusion having been arrived at on the following grounds:—The hydrogenised acid, $\text{C}_8\text{H}_{14}\text{O}_2$, obtained by reducing paramethylenedihydrobenzoic acid does not agree in properties with any of the isomeric hexahydroparatoluic acids, and the product of incomplete reduction is found to be quite unlike its isomeride, Δ^1 -tetrahydroparatoluic acid (preceding abstract). On the other hand, since paratoluic acid is formed when 2HBr are eliminated from the dihydrobromide of paramethylenedihydrobenzoic acid, it is clear that the latter must belong to the series of hydrogenised paratoluic acids, especially as, on reduction, it yields Markovnikoff's liquid hexahydroparatoluic acid. Moreover, although the existence of an unsaturated dihydrobromide appears inconsistent with the presence of only two double linkings in the original substance, it is reasonable to suppose that the central methylene group is but loosely attached. Of the carbon atoms to which it is united, one occupies the para-position relatively to the carboxyl group, three alternatives offering themselves in the choice of a position for the second, as represented by the following types:



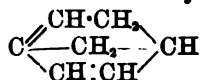
Evidence is brought forward against the first and second of these, the acceptance of the third being quite justified by its complete accordance with the results of the authors' experiments. Of the two forms,



the latter best explains the formation of Δ^1 -tetrahydroparatoluic acid

by the displacement of hydrogen by bromine in the intermediate Δ^3 -dihydrobromide. Finally, in regard to the breaking-down of the molecule, this can obviously take place either at a linking common to both pentamethylene systems, giving rise to hydrogenised paratoluic acids, or at some point in the periphery, in which case a substituted pentamethylenecarboxylic acid is formed.

The analogy existing between anhydroecgonine and tropidine, if extended to paramethylenedihydrobenzoic acid and tropilidene, suggests the representation of the latter by the formula



(compare Merling, Abstr., 1892, 359).

The following facts appear for the first time:—The *tetrabromide* of paramethylenedihydrobenzoic acid, $\text{C}_7\text{H}_4\text{Br}_4\text{COOH}$, is obtained pure by repeated crystallisation from a mixture of formic and glacial acetic acids, and melts at $174-175^\circ$; its alkaline solution immediately decolorises potassium permanganate, indicating its unsaturated character.

$\Gamma^a\text{-}\Delta^3\text{-1}$: 4-Ethylcyclopentenecarboxylic acid, $\text{CHEt} < \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ \text{CH} : \text{CH} \end{array}$,

obtained by the reduction of paramethylenedihydrobenzoic acid with sodium amalgam at the ordinary temperature, has already been fully described as "tetrahydroparatoluic acid" (Abstr., 1893, i, 713).

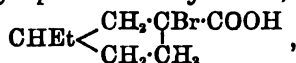
$\Gamma^b\text{-}\Delta^3\text{-1}$: 4-Ethylcyclopentenecarboxylic acid was not obtained in the solid state, and could only be distinguished from the foregoing acid by means of the *amide*, which melts at 185° .

$\Delta^1\text{-1}$: 4-Ethylcyclopentenecarboxylic acid, $\text{CHEt} < \begin{array}{c} \text{CH}_2 \cdot \text{C} \cdot \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{CH} \end{array}$, may

be prepared in three ways: the reduction of a hot solution of paramethylenedihydrobenzoic acid, the action of warm caustic alkalis on the $\Gamma^a\text{-}\Delta^3$ -acid, and the removal of 1 mol. HBr from α -brom-1 : 4-ethylcyclopentanecarboxylic acid (see below). It melts at $47-50^\circ$ (compare Abstr., 1893, i, 713), and distils undecomposed at $260-265^\circ$; its behaviour towards bromine and potassium permanganate is similar to that of the preceding acids, from which it may be distinguished however by its stability towards an alkaline solution of potassium ferricyanide.

1 : 4-Ethylcyclopentanecarboxylic (ethylpentamethylenecarboxylic) acid, $\text{CHEt} < \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$, is best prepared by reducing paramethylenedihydrobenzoic acid with sodium dissolved in amyl alcohol. It is a colourless, highly refractive oil, which boils unchanged at $245-248^\circ$ (uncorr.), and does not solidify at -20° . The *silver* salt forms colourless crystals, and the *calcium* salt can be obtained in two modifications. The *amide* melts at 195° ; the *methylic* salt, a colourless oil of powerful odour, boils at $200-202^\circ$.

α -Brom-1 : 4-ethylcyclopentanecarboxylic acid,



obtained by the application of Volhard's bromination process (Abstr., 1888, 129) to the foregoing acid, separates from hot formic acid in colourless, refractive needles which melt at 94° ; when dissolved in soda, carbonic anhydride is evolved. The removal of 1 mol. HBr from this acid by means of hot quinoline, gives rise to Δ^1 -1 : 4-ethylcyclopentenecarboxylic acid.

The dihydrobromide of paramethylenedihydrobenzoic acid has the constitution $\text{CMe} \begin{smallmatrix} \text{CHBr} \cdot \text{CH}_2 \\ \text{CH} - \text{CH}_2 \end{smallmatrix} \text{CBr} \cdot \text{COOH}$ (compare Abstr., 1893, i, 378), and, when reduced with zinc dust and glacial acetic acid, it gives rise to Δ^3 -tetrahydrotoluic acid, which distils at 243 — 245° ; this yields an amide melting at 117° . By the further reduction of this acid, a liquid hexahydroparatoluic acid is formed, the amide of which melts at 176 — 178° ; it is, therefore, identical with the acid which Markovnikoff obtained by the reduction of paratoluic acid.

M. O. F.

Derivatives of Mandelic acid. By C. A. BISCHOFF and P. WALDEN (*Annalen*, 279, 118—129).—When mandelic acid is heated at 200 — 205° , water and benzaldehyde distil leaving an amorphous mixture in the retort; similar results are obtained on heating the acid in a vacuum or in an atmosphere of carbonic anhydride. On distilling the acid in a current of air, or, preferably, under slightly reduced pressure, benzaldehyde, water, and diphenylmaleic anhydride (Hintze, *Annalen*, 259, 64) come over.

If mandelic acid is heated with phosphorus pentachloride at 100° , mandelic chloride is formed, and, on distillation, phenylchloroacetic chloride is obtained; sodium phenylchloroacetate yields only a small quantity of stilbene (?) on distillation. No dianhydride of the constitution $\text{CHPh} \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \text{O} \cdot \text{CO} \end{smallmatrix} \text{CHPh}$ was obtained in any of the above reactions.

Mandelic anilide is easily prepared by heating the acid with aniline at 180 — 190° ; it melts at 151 — 152° , not at 146° (compare Reissert and Kayser, Abstr., 1891, 438; Biedermann, Abstr., 1892, 473). If the mixture of acid and aniline is treated with phosphorus pentachloride, phenylchloroacetanilide, $\text{CHPhCl} \cdot \text{CO} \cdot \text{NHPh}$, is obtained; it crystallises in small, colourless needles, and melts at 151.5 — 152.5° . On reduction with sodium amalgam, it yields phenylacetanilide, $\text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{NHPh}$, which forms colourless leaflets melting at 116° , and may also be prepared by heating phenylacetic acid with aniline.

Mandelic orthotoluidide, $\text{OH} \cdot \text{CHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, crystallises well, and melts at 72° ; on treatment with phosphorus pentachloride, it yields phenylchloroacetorthotoluidide, $\text{CHPhCl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, which melts at 123 — 125° .

Mandelic paratoluidide melts at 172° , and phenylchloroacetoparatoluidide at 142° ; the latter, on reduction with sodium amalgam, yields phenylacetoparatoluidide, which melts at 132 — 133° .

Mandelic α -naphthalide, $\text{CHPh}(\text{OH}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$, forms colourless crystals melting at 140° , whilst the isomeric β -naphthalide crystallises in colourless, feathery leaflets melting at 189° .

W. J. P.

Allocinnamic acid. By C. LIEBERMANN (*Ber.*, 27, 2037—2051).—Making use of J. Wislicenus' method of bromination of unsaturated acids (*Abstr.*, 1893, i, 135), the author has improved the yield of methylic allocinnamate dibromide, and succeeded in isolating allocinnamic acid dibromide.

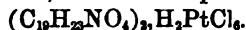
Allocinnamic acid dibromide melts at 91—93°, and differs from the stereoisomeric cinnamic dibromide in being readily soluble in cold carbon bisulphide and in benzene. It forms a clear solution with sodium hydroxide, and if excess of alkali is used, bromocinnamene is eliminated, identical with that obtained from the isomeric dibromide; this change also occurs on boiling with water. The allo-compound is less stable than cinnamic acid dibromide and its solution in sodium hydroxide, although not immediately decolorising potassium permanganate, produces this effect more rapidly than the isomeric modification.

Allocinnamic acid dichloride, which has not been obtained in a crystalline form, is prepared in an analogous manner by means of chlorine dissolved in carbon bisulphide. Like the preceding compound, it is accompanied by a considerable quantity of the cinnamic variety, cold carbon bisulphide affording, as in the previous case, an easy means of separation.

The *cinchonidine salt*, $C_{19}H_{22}N_2O, C_6H_5Br_2O_3$, has been the means of separating allocinnamic acid dibromide into its optically active constituents (compare Hirsch, this vol., i, 334). The maximum rotations obtained were $[\alpha]_D = +10^\circ$ and -71° , but the former does not represent the optical activity of the pure dextro-acid, as this undergoes decomposition on boiling its solution in benzene, with formation of α -bromocinnamic acid. An attempt to prepare a racemic modification by mixing equal weights of cinnamic acid dibromide ($[\alpha]_D = +64^\circ$) and allocinnamic acid dibromide ($[\alpha]_D = -70^\circ$), dissolved in ether, led to a negative result.

Allocinnamic anhydride is prepared by boiling 8 parts of acetic anhydride with 5 parts of allocinnamic acid for 10 minutes. It forms a colourless oil, which, when heated or allowed to remain for some months in an exsiccator, is transformed into cinnamic anhydride.

Allocinnamylcocaine is obtained from allocinnamylecgonine by saturating its solution in absolute methylic alcohol with hydrogen chloride; it occurs as an oil, and forms a *platinochloride*,



Allocinnamylcocaine is decomposed by dilute acids with formation of ecgonine, methylic alcohol, and allocinnamic acid.

The crystallographic examination of allocinnamic acid has been reopened (compare *Abstr.*, 1890, 1417); new forms have been observed, and results have been obtained which lead the author to conclude that this acid is identical with isocinnamic acid (*Abstr.*, 1890, 494), although the description of the latter is too incomplete to confirm this opinion.

M. O. F.

Derivatives of Veratric acid and of Veratrol. By W. HEINISCH (*Monatsh.*, 15, 229—234).—When dimethylprotocatechuic

acid (veratric acid), $C_6H_3(OMe)_2COOH$, is treated with nitric acid, it is converted into nitrodimethylprotocatechuic acid and mono- and dinitrodimethylcatechol. The nitro-acid, separated from the product by extraction with dilute ammonia, melts at $187-188^\circ$.

When nitrodimethylprotocatechuic acid is reduced with the theoretical quantity of stannous chloride and hydrochloric acid, it is converted into amidodimethylcatechol, $C_6H_3(OMe)_2NH_2$. This crystallises in slender, yellow crystals, melts at 80° , and is identical with the compound obtained by the reduction of mononitrodimethylcatechol; the latter melts at 91° . The *platinochloride* is a crystalline, yellow precipitate, and melts at 208° .

Dinitrodimethylcatechol melts at $128.2-128.3^\circ$, and is identical with the compound obtained by nitrating dimethylcatechol (veratrol) and metahemipinic acid. When reduced with stannous chloride and hydrochloric acid, it is converted into *diamidodimethylcatechol*. The *hydrochloride* of the latter crystallises with $2HCl$, but loses 1 mol. of hydrogen chloride on exposure to air. E. C. R.

Dry Distillation of Calcium Diethylprotocatechuate. By W. HEINISCH (*Monatsh.*, 15, 235-238).—When dry calcium diethylprotocatechuate (65 grams) is distilled, a brown, oily liquid (13 grams) is obtained, from which ethylic diethylprotocatechuate is dissolved on adding potassium hydroxide solution and shaking it with ether, whilst the alkaline solution contains ethylic diethylprotocatechuate. The latter crystallises in white needles, and melts at 163° ; monethylcatechol and a small quantity of a compound which the author believes to be diethylcatechol are also formed, and remain in the alkaline solution. The carbonaceous residue from the distillation contains catechol.

Monethylcatechol is a pale yellow oil, which boils at $240-241^\circ$, and with ferric chloride gives a green coloration, which quickly changes to brown, and is converted into a dirty violet by sodium carbonate. E. C. R.

Dry Distillation of Calcium Trimethylgallate. By H. ARNSTEIN (*Monatsh.*, 15, 295-298).—Calcium trimethylgallate crystallises from water with $1\frac{1}{2}H_2O$. When subjected to dry distillation, it yields a dark brown oil which soon solidifies; if this is treated with ether and dilute sodium hydroxide, methylic trimethylgallate dissolves in the ether; it melts at 81° , and on hydrolysis yields trimethylgallic acid (m. p. 167°). An oily residue was also obtained from the ethereal extract, and this, after boiling with potassium hydroxide, yields trimethylpyrogallol melting at 46° . The alkaline solution was found to contain a small quantity of dimethylpyrogallol; it melts at 50° , and boils at 250° . No definite compound could be separated from the carbonaceous residue. E. C. R.

Action of Ethylic Malonate on Benzylideneacetone. By D. VORLÄNDER (*Ber.*, 27, 2053-2058).—*Ethylic phenyldihydroresorcyate*, $C_{15}H_{16}O_4$, the sodium salt of which is formed when ethylic sodio-malonate acts on benzylideneacetone, is identical with the substance

obtained by Michael and Freer (Abstr., 1891, 914) on heating the additive product from ethylic sodacetoacetate with ethylic cinnamate.

From the mode of formation, the formula $\text{CH}_2\text{CO}\cdot\text{CH}\cdot\text{COOEt}$
 $\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}$ ex-

presses its constitution, ethylic alcohol having been eliminated in the reaction. It crystallises from boiling water in colourless needles, which melt at 143° ; the aqueous solution has an acid reaction, and the substance is readily soluble in caustic alkalis and alkali carbonates. It forms a colourless, unstable, silver salt, and its solution in alcohol is coloured brown by ferric chloride. Phenylhydrazine and hydroxylamine give rise to amorphous derivatives.

Phenylldihydroresorcylic acid, $\text{C}_{13}\text{H}_{11}\text{O}_4$, is obtained by the hydrolysis of the ethylic salt. It melts at 98° , losing carbonic anhydride with formation of *phenylldihydroresorcinol*, $\text{C}_{12}\text{H}_{10}\text{O}_2$, which is most conveniently prepared by boiling ethylic phenylldihydroresorcyate for several hours with aqueous sodium carbonate. It forms colourless plates, which become red at 150° , and melts at 184° , decomposing with evolution of gas; the alcoholic solution becomes reddish-brown on the addition of ferric chloride. When distilled with zinc-dust, diphenyl is liberated, the hydrocarbon being easily recognised by its odour. The *dioxime* melts at 177° ; it is insoluble in sodium carbonate, but dissolves in caustic alkalis, reducing Fehling's solution on warming.

β -*Phenyl- γ -acetobutyric acid*, $\text{C}_{13}\text{H}_{14}\text{O}_3$, may be obtained either from ethylic phenylldihydroresorcyate by the prolonged action of hydrochloric acid, or by boiling ethylic phenylldihydroresorcinol with acids or alkalis; it forms long prisms, which melt at 83° .

Other unsaturated ketones also react with ethylic malonate, two molecular proportions of which unite with dibenzylideneacetone. The presence of an acetyl-group facilitates the elimination of alcohol from the additive products, and in the case of the compound from benzylideneacetophenone, no intramolecular condensation takes place.

It is found that ethylic cyanacetate may be substituted for ethylic malonate in this action. Thus, from benzylideneacetone, the *nitrile* of phenylldihydroresorcylic acid, $\text{C}_{12}\text{H}_{11}\text{O}_2\cdot\text{CN}$, is obtained, crystallising in prisms which melt at 175° ; a brown coloration is developed with ferric chloride.

In the case of ethylic acetoacetate, the action proceeds somewhat differently, 1 mol. of water being eliminated, with formation of a substance having the formula $\text{C}_{16}\text{H}_{18}\text{O}_3$; this melts at 94° , and gives a green coloration with ferric chloride.

M. O. F.

Alkylhaloids of Quinic acid. By F. STÖHR (*Chem. Centr.*, 1894, i, 428; from *Pharm. Post*, 27, 13).—*Quinic acid methiodide* forms a pale, reddish-brown precipitate, which becomes yellow when dried and powdered; it melts and decomposes at 250° . The *methochloride* yields golden-yellow needles melting at 215° . By treatment with silver nitrate or sulphate, the iodide yields the *methonitrate* and *methosulphate*. The *ethobromide* and *propobromide*, and some alkylbetaines of quinic acid, are also described.

L. T. T.

Orthamidodiphenyl from Fluorene. By C. GRAEBE and A. S. RATEANU (*Annalen*, 279, 257—267).—The preparation of orthamidodiphenyl, either by nitrating diphenyl and reducing the nitro-compound, or by heating aniline with diazoamidobenzene, is not convenient, because the product consists in both cases chiefly of the para-compound. It may be much more advantageously obtained from fluorene; this is first converted into diphenylene ketone by oxidation with acetic acid and sodium dichromate, and the ketone is then fused with potash at about 180—200°, the temperature not being allowed to rise above the latter limit; in this way, it is converted into diphenylorthocarboxylic acid, which boils at 343—344° (corr.). When this acid is treated with phosphorus pentachloride, the chloride is formed, but cannot be obtained pure, as it begins to decompose at 60—70°, with loss of hydrogen chloride, diphenylene ketone being regenerated. The crude mixture of the chloride with phosphorus oxychloride may, however, be utilised for the preparation of the amide of the acid by diluting it with benzene, and passing ammonia into the cooled solution. The amide may also be prepared, the yield being about the same as in the process just described, by heating the sodium salt of diphenylorthocarboxylic acid with ammonium thiocyanate. Diphenylorthocarboxyamide, $C_6H_4Ph\cdot CONH_2$, crystallises in colourless needles, melts at 177°, and may be distilled without decomposing. It is only slowly attacked by alcoholic potash, and is scarcely altered by aqueous potash at 160—170°. Finally, orthamidodiphenyl is obtained by treating the amide with sodium hypobromite solution in the usual way. It boils at 299°. Special attention was paid throughout the series of preparations to the yields obtained, which were as follows:—100 grams of fluorene yielded 90 grams of diphenylene ketone, 80 grams of diphenylorthocarboxylic acid, 65 grams of diphenylorthocarboxyamide, 50 grams of orthamidodiphenyl.

The following observations were also made during the course of the research. Ethylic diphenylorthocarboxylate boils at 314° (Schmitz, 300—305°), whilst the *methyl*ic salt boils at 308°. The *anilide* of diphenylorthocarboxylic acid may readily be obtained by heating the acid with aniline; it crystallises in large prisms melting at 100°.

Orthoacetylamidodiphenyl crystallises from alcohol in colourless prisms melting at 117.5°. *Diphenyl-hydrazine*, $C_{12}H_8\cdot NH\cdot NH_2$, is prepared by diazotising amidodiphenyl and reducing the diazo-compound with stannous chloride and hydrochloric acid; it forms prismatic crystals, melts at 38°, readily reduces Fehling's solution, and forms condensation products with aldehyde and acetone. The *hydrochloride* separates from water in colourless crystals.

A. H.

The Methylacridones and Methylacridines. By C. GRAEBE (*Annalen*, 279, 268—270).—Introductory remarks to the next three abstracts. The derivatives to be described were prepared by the methods previously employed by Graebe and Lagodzinski (*Abstr.*, 1893, i, 649).

A. H.

2-Methylacridone and 2-Methylacridine. By S. KAHN (*Annalen*, 279, 270—275; compare the foregoing abstract).—*Nitropara-*

2 p

tolylanthranilic acid, $C_7H_7 \cdot NH \cdot C_6H_4(NO_2) \cdot COOH$ [= 6 : 3 : 1], is obtained by heating orthochloronitrobenzoic acid [1 : 6 : 3] with paratoluidine. It crystallises from glacial acetic acid in yellow needles, which melt at 262.5° (corr.). The *potassium* salt, $C_{11}H_{11}N_2O_4K + 2\frac{1}{2}H_2O$, forms yellow needles, and the *barium* salt, $(C_{14}H_{11}N_2O_4)_2Ba + 7H_2O$, vermilion coloured crystals. *Amidoparatolylanthranilic acid* separates from alcohol in colourless prisms which readily become coloured; it melts at 220° (corr.). The *hydrochloride* is partially decomposed by boiling water.

Paratolylanthranilic acid, $C_7H_7 \cdot NH \cdot C_6H_4 \cdot COOH$, forms colourless needles melting at 191.5° (corr.); it is soluble in concentrated hydrochloric acid, but is reprecipitated on adding water. The *barium* salt is only slightly soluble in hot water.

2-Methylacridone, $C_8H_4 < \begin{smallmatrix} CO \\ NH \end{smallmatrix} > C_6H_4Me$, is formed when paratolylanthranilic acid is heated on the water-bath with sulphuric acid. It crystallises from alcohol in yellow prisms, melts at 338° (corr.), and is insoluble in aqueous alkalis; its solution in alcohol has an intense blue fluorescence. When it is heated with zinc dust, *2-methylacridine*, $C_8H_4 < \begin{smallmatrix} CH \\ N \end{smallmatrix} > C_6H_4Me$, is formed; this substance has previously been prepared by Bonna (Abstr., 1887, 927) from phenyl-paratoluidine, and by Ullmann (*J. pr. Chem.*, 36, 265) from diamidodimethyltriphenylmethane. When pure, it melts at 134° (corr.); the *chromate*, $(C_{14}H_{11}N)_2H_2Cr_2O_7$, forms yellow prisms, and the *platinochloride* is a yellow, sparingly soluble salt. When methylacridine is treated with sodium amalgam, it is converted into *2-methylhydroacridine*, $C_8H_4 < \begin{smallmatrix} CH_2 \\ NH \end{smallmatrix} > C_6H_4Me$, which crystallises in colourless plates, melts at 157° (corr.), and does not combine with acids. It is readily reconverted into methylacridine by oxidation with chromic acid.

A. H.

4-Methylacridone and 4-Methylacridine. By J. LOCHER (*Annalen*, 279, 275—280; compare the two preceding abstracts).—*Nitroorthotolylanthranilic acid*, $[COOH : NH : NO_2 = 1 : 2 : 5]$, crystallises from alcohol in slender, pale yellow needles melting at 253 — 254° , and is almost insoluble in water. The *sodium* salt crystallises with $3H_2O$, the *potassium* salt with $2H_2O$, whilst the *silver* salt is a brownish-red powder. *Amidorthotolylanthranilic acid* decomposes when heated above 200° , and forms salts with bases and with strong acids. The *hydrochloride* crystallises in colourless plates, and is decomposed when boiled with a large quantity of water. *Orthotolylanthranilic acid* forms colourless crystals melting at 179° , and is sparingly soluble in hot hydrochloric acid. The *silver* salt is a white powder. *4-Methylacridone* crystallises from alcohol in greenish-yellow needles, melts at 345 — 346° (corr.), and may be sublimed in needles. It is readily soluble in hot alcohol, forming a solution which has an intense blue fluorescence.

Dimethylacridone, $C_6H_4 \begin{smallmatrix} CO \\ \diagup \diagdown \\ NMe \end{smallmatrix} C_6H_2Me$, is obtained by the action of methylic iodide and potash on 4-methylacridone, and forms greenish-yellow needles melting at 183—184°. Alcohol dissolves it freely, forming a solution with an intense blue fluorescence.

4-Methylacridine crystallises in needles, melts at 83°, and may be distilled; its vapour attacks the mucous membrane. It dissolves sparingly in hot water, readily in alcohol, and the solutions as well as the solid act on the skin. The salts are yellow, and their solutions exhibit an intense blue fluorescence. The *dichromate* forms yellow needles, and the *picrate* slender, yellow needles, which are insoluble in alcohol. On oxidation with chromic acid, it yields a mixture of acridone and diacridonyl melting at 250°. A. H.

2 : 4-Dimethylacridone and 2 : 4-Dimethylacridine. By V. KAUFMANN (*Annalen*, 279, 281—288; compare the three preceding abstracts).—*Nitro-xylylanthranilic acid*,



is obtained by heating metanitrothochlorobenzoic acid with 1 : 3 : 4-xylylidine. It crystallises from alcohol in yellow needles, and melts and slightly decomposes at 241°. The *potassium* salt crystallises with $1H_2O$, the *barium* salt with $5H_2O$. *Amido-xylylanthranilic acid*, prepared by reducing the nitro-compound with ferrous sulphate and ammonia, crystallises in colourless, microscopic needles, which readily become dark coloured on exposure to air; it melts and slightly decomposes at about 242°. The *hydrochloride* forms yellow needles which are only sparingly soluble in cold water. *Benzamido-xylylanthranilic acid* is a yellow powder which melts at 264—265°, and is moderately soluble in alcohol. *Xylylanthranilic acid* crystallises in colourless needles which rapidly become coloured in the air; it melts at 182°. The *silver* salt is a white powder sparingly soluble in alcohol.

2 : 4-Dimethylacridone, $C_6H_4 \begin{smallmatrix} CO \\ \diagup \diagdown \\ NH \end{smallmatrix} C_6H_2Me_2$, is obtained by sublimation in sulphur-yellow needles, melting at 294°; it is insoluble in aqueous alkalis, but forms a blue fluorescent solution in alcohol. *2 : 4-Dimethylacridine* melts at 71°; it has the characteristic acridine odour, but its vapour does not attack the mucous membrane so violently as that of acridine, whilst the solid substance does not appear to act on the skin. The *hydrochloride* is soluble in hydrochloric acid; the *platinochloride* and *picrate* form yellow crystals.

2 : 4-Dimethylchloracridine, $C_6H_4 \begin{smallmatrix} CCl \\ \diagup \diagdown \\ N- \end{smallmatrix} C_6H_2Me_2$, is obtained by heating dimethylacridone with phosphorus pentachloride. It crystallises in colourless needles, melts at 108°, and is converted into dimethylacridone by boiling with alcohol or water. The *platinochloride* is only sparingly soluble in water. *Dihydrodimethylacridine*, $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \diagdown \\ NH \end{smallmatrix} C_6H_2Me_2$, which crystallises in colourless plates, melting

at 80°, is formed, along with an insoluble substance, which melts at 155—156°, when dimethylacridine or dimethylacridone is treated in alcoholic solution with sodium amalgam. A. H.

Ethereal Salts of Natural Naphthenic acids. By V. MARKOVNIKOFF (*J. Russ. Chem. Soc.*, 25, 654—658).—The methyl salts of the lower natural naphthenic acids were prepared and fractionated with a view to isolate the methyl salt of heptanaphthenic acid (hexahydrobenzoic acid). This salt boils at 181—183°, and the fraction boiling at 180—182° gave numbers, on analysis, not far removed from those required by the formula, a slight excess of hydrogen being attributed by the author to the presence of fatty acids along with the naphthenic acids. J. W.

Hydroxynaphthaquinoneimidobenzoic acid. By D. A. CHAR-DIN (*J. Russ. Chem. Soc.*, 25, 685—687).—Orthoamidobenzoic acid condenses very readily with β -naphthaquinone, giving β -hydroxynaphthaquinoneamidobenzoic acid, $\text{OH}\cdot\text{C}_{10}\text{H}_6\text{O}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, which crystallises in bronze-red scales, and melts at 270—271°. It can be heated to 180° with sulphuric acid without undergoing decomposition. On long-continued boiling with hydrochloric acid, it yields hydroxynaphthaquinone and amidobenzoic acid. On reduction, it yields a colourless substance which oxidises to the original compound if exposed to the air. J. W.

Synthesis of α -Alkyl- β -naphthocinchonic acids: Specific Reaction for Aldehydes. By O. DOEBNER (*Ber.*, 27, 2020—2030; compare this vol., i, 261).—The action which takes place when an aldehyde is heated with pyruvic acid and β -naphthylamine dissolved in alcohol has been applied to all classes of aldehydes, and is found to take effect in every case except that of hydroxyaldehydes such as glycerose, in which an hydroxyl group is linked to the carbon atom to which the aldehydic residue is attached. The author regards this circumstance as explaining the fact that the test does not apply to those sugars which are represented as aldehydes.

β -Naphthocinchonic acids have been prepared from the following aldehydes:—Acetaldehyde, propaldehyde, isobutaldehyde, isovaleraldehyde, cænanthaldehyde, crotonaldehyde, tiglic aldehyde, citronellic aldehyde, citral, aldol, furfuraldehyde, salicylaldehyde, anisaldehyde, vanillin, piperonal, and cuminaldehyde. On heating the several naphthocinchonic acids above their melting points, the corresponding α -alkyl- β -naphthoquinolines are formed.

The α -alkyl- β -naphthocinchonic acids possess the salt-forming properties both of acid and of base, yielding not only metallic salts, but also hydrochlorides and platinochlorides. M. O. F.

Hydroxyanthraquinones. By H. OFFERMANN (*Annalen*, 280, 1—35).—It has long been known that when the condensation of metahydroxybenzoic acid is effected by means of sulphuric acid

diluted with 10 per cent. of water, 1 : 4', 2 : 3' and 2 : 1'-dihydroxy-anthraquinones are formed. Employing concentrated acid, the author has obtained exclusively a sulphonic acid which is split up into anthraflavic and sulphuric acids when heated in a closed tube with hydrochloric acid, and which yields flavopurpurin when fused with potash, showing it to be 1 : 2 : 3'-dihydroxyanthraquinonesulphonic acid or sulphoanthraflavic acid; when this acid is heated with hydrochloric and dilute sulphuric acids at 250°, metahydroxybenzoic acid is formed, together with a small quantity of anthraflavic acid.

Studying the action of fused potash on 1 : 4'- and 1 : 3'-anthraquinonedisulphonic acids, Dehnst observed that the intermediate products, anthranfin and chrysazin, undergo a change of a two-fold character, hydroxybenzoic acids being formed, accompanied on the other hand by hydroxychrysazin. It is found that whilst anthraflavic acid under similar treatment does not give rise to definite products, 1 : 2'-dihydroxyanthraquinone when fused with a mixture of caustic soda and potash yields, according to temperature, either anthrapurpurin or an isomeric trihydroxyanthraquinone (compare Dehnst, *Ber.*, 12, 1293). The latter compound is obtained when the temperature of the mixture is gradually raised from 190° to 300°, and forms small red needles, the properties of which correspond in all respects with those described by Dehnst (*loc. cit.*); the *acetyl* derivative, $C_{14}H_5O_2(OAc)_3$, crystallises from glacial acetic acid in hexagonal plates which melt at 205°.

Although hydroxybenzoic acids are not formed by fusing anthraflavic acid and 1 : 2'-dihydroxyanthraquinone with potash, this decomposition is effected when the anthraquinonedisulphonic acids, from which these compounds are derived, are made the starting point of the reaction. Treated in this way, 2 : 3'-anthraquinonedisulphonic acid yields protocatechuic acid, meta- and parahydroxybenzoic acids, and most probably 1 : 2 : 3-dihydroxybenzoic acid. Contrary to the statement of Hlasiwetz and Barth (*Annalen*, 134, 276), the first-named of these may be easily separated from parahydroxybenzoic acid, the basic lead salt of which is soluble in water. In like manner, 2 : 2'-anthraquinonedisulphonic acid yields anthrapurpurin, which at a higher temperature becomes converted into the above-mentioned isomeride, together with protocatechuic and metahydroxybenzoic acids, unaccompanied, however, by parahydroxybenzoic acid.

The paper concludes with the theoretical consideration of these results and their significance in determining the constitution of polyhydroxyanthraquinones.

M. O. F.

Constitution of Euxanthone. By S. V. KOSTANECKI (*Ber.*, 27, 1989—1993).—From Graebe's investigations, the hydroxyl groups in euxanthone appear to occupy the positions 3—4', the author's synthesis indicates the constitution 5—4'. The *methyl-5-hydroxyxanthenes*, formed by the action of resorcinol on the three commercial hydroxytoluic acids in presence of acetic anhydride, are purified by means of their crystalline *sodium salts*, from the methyl-3-hydroxyxanthenes, which are formed in very small quantity, and from the dimethylxanthenes. 2' : 5-Methylhydroxyxanthone crystallises in

yellow needles melting at 152°. 3' : 5-Methylhydroxyxanthone and 4' : 5-methylhydroxyxanthone are deposited in yellow plates, and melt at 176° and 135° respectively. 1 : 3 : 5-Methyldihydroxybenzene and 1 : 2 : 4-methyldihydroxybenzene combine with salicylic acid to form methyl-5-hydroxyxanthenes, the yield of methyl-3-hydroxyxanthenes is extremely small. 4 : 5- or 2 : 5-Methylhydroxyxanthone crystallises in yellow needles melting at 112°. 1 : 3 : 5-Methyldihydroxybenzene combines with the hydroxytoluic acids to form the following: 2' : 3 : 5-dimethylhydroxyxanthone, 3' : 3 : 5-dimethylhydroxyxanthone, and 4' : 3 : 5-dimethylhydroxyxanthone; these crystallise in yellow needles, and melt at 145°, 139°, and 169° respectively. Dimethyl-3-hydroxy-derivatives were formed in very small quantity only. In all these cases, the acid radicle attacks the phenol between the hydroxyl groups, therefore isoeuxanthone, from resorcinol and 2 : 4-dihydroxybenzoic acid, should be either 3 : 3'- or 5 : 3'-dihydroxyxanthone; that the latter formula is correct is shown by the production of a monomethyl ether, which crystallises in yellow plates, melts at 143—144°, yields a crystalline sodium salt, and an acetyl derivative, crystallising in colourless plates, and melting at 150°.

Euxanthone methyl ether, $\text{OMe} \cdot \text{C}_{13}\text{H}_8\text{O}_5 \cdot \text{OH}$ [$\text{OMe} : \text{OH} = 4' : 5$], is prepared in a similar manner, and crystallises in yellow plates melting at 129°. The sodium salt is crystalline, and insoluble in alkalis.

Attempts to prepare 2 : 4 : 5 : 4'-dimethyldihydroxyxanthone from 2 : 5-dihydroxybenzoic acid and 1 : 3 : 4 : 6-dimethyldihydroxybenzene were not very successful, only a small quantity of a compound was formed, which gave the characteristic euxanthone reaction with sodium amalgam. 1 : 3 : 5-Methyldihydroxybenzene and 2 : 5-dihydroxybenzoic acid, in presence of zinc chloride, combine to form 3 : 5 : 4'-methyldihydroxyxanthone, which crystallises, and sublimes in long, yellow needles, melts at 252°, and resembles euxanthone in its behaviour towards sodium amalgam. The diacetyl-derivative crystallises in small, colourless needles melting at 163°. J. B. T.

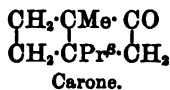
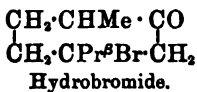
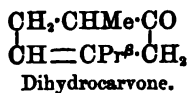
Hydroxyxanthone Derivatives and Maclurin. By E. KÖNIG and S. V. KOSTANECKI (*Ber.*, 27, 1994—1997).—The following brom-hydroxyxanthenes were prepared by the action of bromine on the hydroxyxanthone in glacial acetic acid solution, for the sake of comparing them with the corresponding derivatives of yellow vegetable colouring matters. *Dibromo-5-hydroxyxanthone* crystallises in long, yellow, lustrous needles melting at 222°. *Dibromo-4-hydroxyxanthone* forms pale yellow needles melting at 207°. The sodium salt is intensely yellow. *Dibromo-3-hydroxyxanthone* crystallises in long, colourless needles, and melts at 269—272°; the sodium salt is also colourless. *Dibromo-2-hydroxyxanthone* is deposited in colourless needles; it melts at 274—276°, and dissolves in alkalis with a yellow colour. *Dibromo-5 : 3-dihydroxyxanthone* forms pale yellow needles melting at 245°. *Dibromo-5 : 4'-dihydroxyxanthone* (euxanthone) crystallises in yellow needles, and melts at 280°. *Dibromo-5 : 4'-hydroxymethoxyxanthone* crystallises in yellow needles, melts at 196°, and is also formed by the action of methylic iodide and potassium hydroxide on the preceding compound. The sodium salt is yellow, and insoluble. *Tetrabromo-*

5 : 3'-*dihydroxyxanthone* (isoeuxanthone) was only obtained in small quantity; it crystallises in pale yellow needles, and melts at 280°. The following four benzoyl derivatives crystallise in colourless needles: *benzoyl-5-hydroxyxanthone*, melting at 206·5°; *benzoyl-4-hydroxyxanthone*, melting at 151°; *benzoyl-3-hydroxyxanthone*, melting at 147°; *benzoyl-2-hydroxyxanthone*, melting at 172°.

Maclurin, which is readily resolved into phloroglucinol and 3 : 4-dihydroxybenzoic acid, also appears to be a hydroxyketone; it yields a *pentabenzoyl-derivative*, which forms colourless, glittering crystals melting at 153—156°.

J. B. T.

Orientation in the Terpene Series: the Terpenones of the Carvone Group. By A. BAEYER (*Ber.*, 27, 1915—1923; compare this vol., i, 92, 252, 297).—Dihydrocarvone unites with hydrogen bromide in acetic acid solution, forming an additive compound, which, on treatment with alkalis, loses hydrogen bromide, yielding an isomeride of dihydrocarvone, to which the name *carone* has been given. It is a colourless oil, having an odour resembling that of camphor and peppermint, and boils at about 210°, undergoing slight decomposition. Its *oxime* is liquid, but with semicarbazide it yields a crystalline derivative, $C_{10}H_{16} \cdot N \cdot NH \cdot CO \cdot NH_2$, which forms acute needles or long prisms, and melts at 169°. Another crystalline derivative, obtained by the action of amidoguanidine picrate, separates from alcohol in concentric groups of prisms or flat plates. Carone is very stable towards potassium permanganate, and is only very slowly attacked by bromine; it differs, therefore, from other compounds hitherto obtained by the action of alkalis on brominated hydrobenzene-derivatives, which have, one and all, shown reactions consistent with the supposition that they contain an ethylene linking. The above formation of carone renders untenable the author's previous supposition that compounds containing ethylene linkings were invariably formed under these circumstances. The most probable supposition as to the constitution of carone is that it contains a para-linking, its constitution being analogous to that proposed by Semmler for tanacetone (this vol., i, 339). The most probable formulæ for dihydrocarvone, its hydrobromide, and carone are as follows.



The compound obtained by the action of bromine on carone has not been obtained crystalline, but, as no hydrogen bromide is evolved, it must be an additive compound. If the above formula is correct, it must be the ketone of dipentene dihydrobromide; experiments to ascertain whether this is so are now in progress. Hydrobromic acid converts carone into the hydrobromide from which it was prepared.

When dihydrocarvone is treated with sulphuric acid at 0°, it is converted into the compound termed *carveol* by the author, and already obtained by Wallach (this vol., i, 44), by heating the oxidation pro-

duct of solid terpineol with dilute sulphuric acid; carone, likewise, yields the same compound on heating, so that carveol appears to be the final product of intramolecular change of several members of this series. The same series of reactions which is employed for the conversion of carvone into isocarvoxime, brings about the conversion of dihydrocarvone into carveol. For this purpose, dihydrocarvoxime is treated with hydrogen bromide in acetic acid solution, and the product subjected to the action of potash in methylic alcohol solution, carveoloxime being thus obtained.

Eucarvone, on reduction with sodium in alcoholic solution, yields the corresponding *dihydroeucarveol*, $C_{10}H_{18}O$, which has a camphor-like odour, boils at $109-110^{\circ}$, under a pressure of 21 mm., and is still an unsaturated compound. When oxidised with chromic acid, it yields a ketone, having the composition of a terpenone, termed *dihydroeucarvone*, $C_{10}H_{16}O$; this has a faint odour of peppermint and camphor, boils at $86-88^{\circ}$, under 14 mm. pressure, and yields an oily oxime. The latter forms a crystalline *hydriodide*, which may be obtained in colourless prisms; it melts at 161° , and is only slightly soluble in the ordinary solvents. The *semicarbazide compound* crystallises in plates, and melts at $189-191^{\circ}$. Dihydroeucarvone also readily yields a crystalline *nitroso-compound*, which forms large prisms, melts and decomposes at $119-120^{\circ}$, and is probably a tertiary derivative similar to that of menthone (this vol., i, 522).

Semicarbazide may in many cases be employed with advantage in the isolation of ketones, as the derivatives are often crystalline when the oximes and hydrazones are oils. The semicarbazide compounds are also very readily resolved into their components by the action of dilute acids. In cases where the semicarbazide does not give good results, amidoguanidine may be employed, the product being isolated as the picrate.

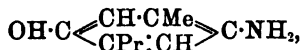
The following table gives the melting points and crystalline forms of the semicarbazide compounds of the carvone group.

	Melting-point.	Crystalline form.
Tanacetone.	171—172°	Acute prisms.
Carone	167—169	Long needles and prisms.
Dihydrocarvone..	187—188	Slender prisms with blunt ends.
Dihydroeucarvone	189—191	Thin plates.
Carveol	202—205	Spindles or six-sided plates.
Carvotanacetone .	177—179	Rhombic tablets and oblique prism.
Carvone	162—163	Six-sided plates.
Eucarvone	183—185	Concentric aggregates of prisms.

H. G. C.

The Carvone Series. By O. WALLACH and H. SCHRADER (*Annalen*, 279, 366—390).—In the preparation of carvoxime, for which an excess of hydroxylamine has to be employed, a compound, of the formula $C_{10}H_{14}NOH.NH_2.OH$, is obtained as a thick syrup, which crystallises very slowly, and then melts at $174-175^{\circ}$.

When carvoxime is dissolved in sulphuric acid, it undergoes molecular change, and is converted into *paramidothymol*,



which melts at 173—174°. The constitution of this substance is proved by the facts that when its diazo-salts are boiled with water, thymoquinone is formed, whilst with alcohol, thymol itself is produced.

It is probable that the carvoxime, $\text{HC}\begin{matrix} \text{CH}\cdot\text{CHMe} \\ \text{CPr}=\text{CH} \end{matrix}\text{>C}\cdot\text{NOH}$, first passes into the form of cymylhydroxylamine,



which is then converted by the action of the acid into amidothymol.

When carvoxime is heated with strong aqueous potash at 230—240°, carvacrylamine, $\text{C}_{10}\text{H}_{15}\text{N}$, is obtained. This substance, when treated with acetic anhydride, is converted into a *diacetyl*-derivative, which melts at 66°. The conversion of the carvoxime into this base proceeds at a lower temperature in the presence of stannous chloride, and is probably due to the action of the potash on the cymylhydroxylamine, into which the oxime may be supposed to pass.

Reduction of Carvone.—When carvone is reduced by means of alcohol and sodium, dihydrocarveol is formed, whilst if dilute potash or acetic acid and zinc dust are used, dihydrocarvone, identical with the substance obtained by the oxidation of dihydrocarveol, is formed. In addition to this ketone, a substance of the empirical formula, $\text{C}_{10}\text{H}_{15}\text{O}$, is produced, which is probably the *pinacone* of the series; it crystallises in large prisms, which have a vitreous lustre and melt at 148—149°. Both the pinacone and dihydrocarvone derived from *d*-carvone are lævorotatory. Dihydrocarvoxime (Abstr., 1893, i, 595) crystallises in two forms, sparingly soluble needles and transparent prisms, melting at 88—89°. When left in contact with alcohol, the needles gradually become converted into prisms. When the oxime is treated with sulphuric acid, it is converted into *isocarvoxime*, which melts at 87—88°, crystallises only in prisms, and is much more stable towards hot dilute sulphuric acid than the true oxime. Dihydrocarvoxime (*d*- or *l*-) readily combines with hydrogen bromide in acetic acid solution, forming *bromotetrahydrocarvoxime*, $\text{C}_{10}\text{H}_{17}\text{Br}\cdot\text{N}\cdot\text{OH}$, which crystallises well from ether, and melts and decomposes at 109°. Both forms of the true oxime yield this compound, whilst the iso-oxime does not unite with hydrogen bromide under these conditions. When this hydrobromide is melted, it loses water and is converted into the hydrobromide of carvacrylamine; this reaction indicates the close relation which exists between the isomeric compounds, dihydrocarvone and thujone (Abstr., 1893, i, 107).

The fraction of thuja oil, boiling at 220—230°, contains a hydrocarvone, which yields an oxime melting at 93—94°, and easily forms a compound with hydrogen sulphide melting at about 94—95°. It is possible that this substance is identical with the carvo-tanacetone obtained by Semmler (this vol., i, 339). The isomeride of

dihydrocarvone, obtained by oxidising dihydrocarveol (this vol., i, 45), reacts with hydroxylamine, giving a mixture of two isomeric substances, one of which melts at 111—112°, whilst the other melts at 164—165°; the nature of the latter has not yet been decided.

The ketone previously described (this vol., i, 45), as prepared indirectly from pinylamine, may be known as *isocarvone*; it boils at 222—224°, has a sp. gr. of 0.989 at 19°, and a specific refractive index $n_D = 1.5067$. It is therefore of the same degree of saturation as carvone, and, like it, combines with hydrogen sulphide.

The characterisation of the carvones and hydrocarvones by means of their oximes is very unsatisfactory, as these substances resemble one another in melting point, &c., very closely. The bromides have not hitherto been obtained crystalline, but may be prepared in this state by dissolving the substance in an acetic acid solution of hydrogen bromide, and adding bromine. Dihydrocarvone, treated in this way, yields the *dibromide*, $C_{10}H_{16}O, Br_2$, in lustrous crystals. The active modifications of this bromide melt at 69—70°, whilst the racemic modification melts at 96—97°. *Carvone tetrabromide*, $C_{10}H_{14}O, Br_4$, may be prepared in a similar manner. The active compound melts at 119—121°, the racemic at 74—76°. A. H.

Sesquiterpenes. By O. WALLACH and F. E. TUTTLE (*Annalen*, 279, 391—397; compare Abstr., 1893, i, 101).—*Caryophyllen nitrosate*, $C_{15}H_{24}N_2O_4$, crystallises from benzene in slender needles melting at 148—149°. With piperidine, it yields a *nitrolamine*,



which forms transparent crystals melting at 141—143°. The *urethane of caryophyllen alcohol*, $NHPh \cdot COOC_{15}H_{25}$, crystallises in needles melting at 136—137°. The *acetate*, $C_{15}H_{25} \cdot OAc$, may be prepared by digesting the iodide with sodium acetate and acetic acid. The previously described hydrocarbon, $C_{30}H_{50}$, when pure, crystallises in large prisms, and melts at 144—145°.

Patchouli alcohol, $C_{15}H_{26} \cdot OH$, is converted by even the feeblest dehydrating agents into *patchoulene*, $C_{15}H_{24}$, which boils at 254—256°; its sp. gr. at 23° is 0.939, and its refractive index $n_D = 1.50094$, so that it only contains one ethylene linking. The alcohol is probably tertiary.

The substance known commercially as champacol, obtained from Champaca wood by distillation with steam, is identical with a product previously obtained from guaiac-wood. The pure compound, which may be called *guaiol*, melts at 91°, boils at 288°, and is an alcohol. It is not altered by dilute sulphuric acid, and gives a deep red coloration with phosphoric anhydride. When heated with zinc chloride, and then distilled in steam, a blue oil passes over. This has the formula $C_{15}H_{24}$, and boils at 124—128°; its sp. gr. at 20° is 0.910, and its refractive index $n_D = 1.50114$. The origin of the blue colour has not yet been ascertained. A. H.

Isomeric Camphoric acids. By O. ASCHAN (*Ber.*, 27, 2001—2012).—Thirteen modifications of camphoric acid have been described at various times, namely:—(1), ordinary dextrocamphoric acid;

(2), Chautard's *lævocamphoric acid*; (3), Chautard's *paracamphoric acid*, the racemic compound of Nos. 1 and 2; (4), Chautard's inactive *camphoric acid* from diethylic *paracamphorate* (No. 3); (5), Wreden's *mesocamphoric acid*, which is apparently inactive; (6), Wreden's *i-camphoric acid* (m. p. 160°); (7), Armstrong and Tilden's *i-camphoric acid* (m. p. 202°); (8), Jungfleisch's *i-camphoric acid* formed by the action of water at 280° on No. 1; (9), *lævoisocamphoric acid*; (10), Jungfleisch's *i(?)*-acid formed by the action of water on No. 2, and corresponding with No. 5; (11), Jungfleisch's *dextroisocamphoric acid*; (12), *i-camphoric acid*, the racemic compound of Nos. 9 and 11; (13), Marsh and Stockdale's *i-camphoric acid*. On comparison, it is found that only six of these, that is Nos. 1, 2, 3, 9, 11, and 12, are definite compounds; the remainder are either identical with one of these six, or are mixtures of varying composition. The three *camphoric acids*, Nos. 1, 2, and 3, are sharply differentiated from the three *isocamphoric acids* by the ease with which they form anhydrides, they have, therefore, the *maleinoid* or *cis* configuration, the *isocamphoric acids* having the *fumaroid* or *cistrans* configuration. In both series, the two active acids are identical in chemical and physical properties, with the exception of the optical activity, which is equal and opposite; the active *camphoric acids* melt at 187° ; the active *isocamphoric acids* at $171-172^{\circ}$. *i-Camphoric acid* melts at $202-203^{\circ}$; *i-isocamphoric acid* at 191° ; both are less soluble than the active acids from which they are formed and into which they are not resolved by crystallisation; they are optically inactive. Mixtures of equal parts of an acid from each series with opposite activities (*mesocamphoric acids*) have variable melting points much below those of their components, they have a feeble optical activity, and are resolved into their constituents by fractional crystallisation, and quantitatively by the action of acetic chloride, which readily converts the *camphoric acids* into anhydrides, but is without action on the *isocamphoric acids*. The conversion of an active acid of one series into that of another (*cis* into *cistrans* or *vice versa*) by the action of water at high temperatures only proceeds to the extent of about 50 per cent., and the acid produced has the opposite sign of activity to that of the original one; all attempts, however, to convert an active acid into the racemic form, or into its complementary active modification of the same series, have been unsuccessful. The reaction takes place more quickly at a lower temperature, and the yield is increased, by the use of a mixture of glacial acetic acid and concentrated hydrochloric acid instead of water. The *isocamphoric acids* may also be converted into *camphoric acids*, with opposite activities, by dry distillation, anhydrides being first formed, but the inverse change (*cis* into *cistrans*) does not take place. The same change, which applies to each series, is produced by the action of bromine on the acid and the subsequent reduction of the brominated product with zinc dust and glacial acetic acid. From these results, it appears that *camphoric acid* contains two asymmetrical carbon atoms; the theoretical consequences of this view, and its bearing on the question of the constitution of *camphor* and *borneol* will be considered subsequently.

Of the remaining seven "camphoric acids" (see above), two, Nos. 5 and 10, have been previously shown by Friedel and Jungfleisch to be mixtures. Chautard's paracamphoric acid (No. 4) is a mixture of i-camphoric acid (3 parts) and i-isocamphoric acid (1 part). Wreden's inactive acid (No. 6) consists of dextrocamphoric acid and lævoisocamphoric acid. Jungfleisch's inactive acid (m. p. 280° , No. 8) is identical with Wreden's meso-acid, and consists of a mixture of dextrocamphoric acid and lævoisocamphoric acid. Armstrong and Tilden's, and Marsh and Stockdale's inactive acids (Nos. 7 and 13) are identical with i-camphoric acid (No. 3). Full details of the preparation, purification, and methods of identification of these compounds are given in the original paper. For purposes of comparison, the three camphoric anhydrides, and bromo- and chloro-camphoric anhydrides, have been prepared, and also the three camphanic acids; the activity of these compounds is of opposite sign to that of the acid from which they are derived. Dextro- and lævo-camphoric anhydrides in chloroform solution at 20° are inactive, in benzene solution optically active; this affords an interesting confirmation of Van't Hoff's statement that in spite of the presence of asymmetrical carbon atoms, a compound may appear inactive, the activity being, however, rendered apparent by change of temperature or of solvent.

J. B. T.

Scammony Resin. By H. SPIRGATIS (*Arch. Pharm.*, **232**, 241—243).—The author cannot admit that the analyses of the barium salt obtained from scammony resin, which were made first by himself and then by Mayer, are incorrect as suggested by Poleck (*Abstr.*, 1893, i, 225).

A. G. B.

Investigation of the Resin of Jalap. By N. KROMER (*Chem. Centr.*, 1894, i, 634—636; from (*Pharm. Zeit. Russ.*, **33**, 1—5, 17—21, 33—37, 49—53, 65—69, 81—85, 97—99).—Mayer ascribed to that part of the resin of the true jalap (*Ipomoea Purga*, Hayne, or *Convolvulus purga*, W.), which is insoluble in ether, the name convolvulin, and the formula (?) $C_{72}H_{80}O_{36} + Aq$, and to the analogous compound from the spurious jalap the name jalapin. The author has re-examined convolvulin and its derivatives.

Convolvulin forms a colourless, amorphous mass which becomes electrified when rubbed. It is soluble in alcohol and in acetic acid, but insoluble in ether or light petroleum. Its reaction is neutral, and it is coloured red to brownish-red by concentrated sulphuric, nitric, or hydrochloric acid. It melts at 140 — 148° , and gives a rotation $[\alpha]_D = -36.9^{\circ}$, and a mol. wt. of 1140—1393. From its analysis and chemical behaviour, the author believes its true formula to be $C_{61}H_{108}O_{27}$.

When treated with bases, barium hydroxide for instance, it yields convolvulinic and methylethylacetic acids. *Convolvulinic acid*, $C_{28}H_{52}O_{14}$, is a white, hygroscopic powder melting at about 180° , and having a rotation $[\alpha]_D = -31.3^{\circ}$. The barium salt, $Ba(C_{28}H_{51}O_{14})_2 + 2H_2O$, is yellow and amorphous. It is a monobasic acid which forms neutral and basic salts, and also combines with convolvulin.

When hydrolysed with 10 per cent. sulphuric acid, convolvulinic acid is decomposed into a non-crystalline glucose, $C_6H_{12}O_6$, and convolvulinolic acid (m. p. 46°), a monobasic acid isomeric with jalapinic acid. The convolvulinol obtained by Meyer in this reaction was probably impure convolvulinolic acid. The glucose, on oxidation, yields paragluconic acid.

L. T. T.

The Wall-lichen (*Parmelia parietina*). By R. KOBERT and W. LILIENTHAL (*Chem. Centr.*, 1894, i, 471—472; from *Zeit. Oester. Apoth. Ver.*, 48, 30—38).—The colouring matter, which the authors consider to be the active principle of this lichen, is very superficially distributed, and may be extracted by means of benzene without destroying the lichen. It crystallises in small, golden-yellow needles which are soluble in alkalis with blood-red coloration. It is more soluble in the ordinary organic solvents than chrysophanic acid, which it was thought to contain by Rochleder and Heldt. The authors consider this colouring matter to be a dihydroxyanthraquinone, and propose for it the name *chrysophycin*. It is not poisonous, whilst vulpinic acid (with which Bolley considered it to be identical) is poisonous. The colouring matter was termed parietin by Thomsen, and "chrysopykrin" by Stein. The lichen, after extraction of the colouring matter, is not poisonous.

L. T. T.

A New Substance Extracted from Lichens. By G. PATERNO and F. CROSA (*Gazzetta*, 24, i, 297—305).—On extracting the lichen, *Lecanora sulphurea* (Schaer), with ether, a mixture containing a resin, usnic acid, rangiformic acid, and a new substance, $C_{27}H_{30}O_8 \cdot H_2O$, is obtained. The latter is purified by crystallisation from alcohol, benzene, and carbon bisulphide, and is ultimately obtained in white, pearly laminæ melting at $92-93^\circ$; the anhydrous substance separates from benzene in minute crystals melting at $123-124^\circ$. On cooling the molten mass, it becomes vitreous and melts at about 65° ; if this is treated with dilute alcohol, it absorbs water with great development of heat, and yields the hydrate melting at $92-93^\circ$. It is readily soluble in cold caustic alkalis, giving solutions which resinify on exposure to air, whilst the alcoholic solution reduces silver nitrate and Fehling's solution, and gives a violet coloration with ferric chloride. The argento-derivative, $C_{27}H_{30}O_8 \cdot Ag$, is obtained as an unstable, gelatinous, white precipitate, which yields the original substance when treated with dilute hydrochloric acid, boiling water, or ethylic iodide. Molecular weight determinations by the cryoscopic method or by Beckmann's method were valueless, the thermometric rise or fall being so small. On boiling the substance with dilute hydrochloric or hydriodic acid, it yields a dehydration product, $C_{27}H_{28}O_8 \cdot H_2O$, crystallising in colourless, transparent prisms; these effloresce in the air, leaving the anhydrous substance, which melts at $142-143^\circ$. This compound is also obtained by warming a solution of the original substance in concentrated sulphuric acid and precipitating with water, or on treating it with acetic chloride or boiling

with sodium carbonate solution. The dehydration product yields normal caproic acid when fused with potash, but gives no argento-derivative.
W. J. P.

Scoparin. By G. GOLDSCHMIEDT and F. V. HEMMELMAYR (*Monatsh.*, 15, 316—361; Abstr., 1893, i, 601).—Acetylscoparin, which has already been described by the authors, sinters at 242° when pure, and melts at $255\text{--}256^{\circ}$. It forms hemimorphic crystals belonging to the monoclinic system, $a : b : c = 0.8738 : 1 : 1.3454$; $\beta = 77^{\circ} 59'$. The numbers obtained from a long series of analyses and molecular weight determinations show that the compound is *hexacetylscoparin*. *Hexabenzoylscoparin* is a bright, yellow, crystalline compound, and melts at $148\text{--}150^{\circ}$.

Ethylscoparin, $C_{19}H_{16}O_8(OMe) \cdot OEt$, reduces Fehling's solution and ammoniacal silver solution when heated with it on the water bath, but is not altered by boiling with alcohol, differing in this respect from scoparin. The *pentacetyl-derivative* crystallises in aggregates of small, white needles, sinters at 120° , and melts at $140\text{--}141^{\circ}$.

Methylscoparin has not yet been obtained pure. The product crystallises in beautiful, rhombic plates, sinters at 175° , melts at 185° , and, after solidifying, remelts at $252\text{--}253^{\circ}$. The numbers obtained on analysis seem to show that the compound is a mixture of methylscoparin with scoparin, but it does not give the reaction for scoparin with ferric chloride.

Scoparin, when boiled with 6—7 per cent. potassium hydroxide in a reflux apparatus, is partially decomposed with formation of acetovanillone; this crystallises in short, lustrous prisms, melts at 115° , boils at about 300° , and with ferric chloride gives an intense blue coloration. The *acetyl-derivative* forms beautiful, white needles, and melts at $57\text{--}58^{\circ}$. The *hydrazone* crystallises in bright, yellow needles, and melts at 125° . When fused with potassium hydroxide, it yields protocatechuic acid. The authors have also examined the behaviour of scoparin when heated with stronger solutions of potassium hydroxide, and have separated from the product, acetovanillone, vanillic acid, protocatechuic acid, and phloroglucinol. The same decomposition products were obtained by allowing scoparin to remain with 10 per cent. potassium hydroxide in a closed vessel for 286 days. When scoparin is boiled with 12 per cent. potassium hydroxide and the mixture is acidified with phosphoric acid and subjected to steam distillation, formic acid is obtained in small quantity.

Ethylscoparin, when treated with potassium hydroxide (10 per cent.), yields a brown oil, from which ethylvanillic acid (m. p. 193°) is obtained on oxidation with potassium permanganate.

When scoparin is boiled with dilute hydrochloric acid, it yields the compound $C_{20}H_{16}O_8 \cdot \frac{1}{2}H_2O$, which has already been obtained by the action of sulphuric acid; it dissolves in dilute potassium hydroxide, and is precipitated unchanged on acidification; but when boiled with 12 per cent. potassium hydroxide, it yields acetovanillone and small quantities of phloroglucinol.

When scoparin is heated above its melting point, it gives off $3\frac{1}{2}H_2O$, whilst ethylscoparin, under similar conditions, gives off $3H_2O$. Both

compounds are reduced by sodium amalgam, yielding dark red, amorphous compounds, which give violet precipitates with lead acetate. The compound obtained from scoparin, on analysis, gave numbers agreeing with the formula $C_{20}H_{24}O_{10}$ or $C_{20}H_{18}O_9$.

The authors were unable to obtain a hydrazine or oxime from scoparin or ethylscoparin. When scoparin is heated with excess of phenylhydrazine at 100° and the product is washed with chloroform, a bright yellow, crystalline mass is obtained, which darkens at 225° , turns black at 235° , and decomposes violently at 236° . It gradually decomposes on exposure to the air, giving off phenylhydrazine.

Scoparin forms additive compounds with hydrogen chloride, hydrogen bromide, or bromine, which are very easily decomposed. It has absolutely no physiological action.

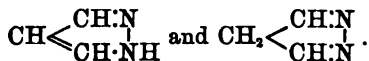
The above results show that the constitution of scoparin may be expressed by the formula $OH \cdot C_6H_3(OMe) \cdot C_{13}H_8O_3(OH)_2$, [$= 1 : 3 : 5$], and that in the group $C_{13}H_8O_3(OH)_2$, there is present an atomic complex which is capable of yielding phloroglucinol when treated with potassium hydroxide.

E. C. R.

Red Pigment of *Pyrrhocoris Apterus*. By C. PHISALIX (*Compt. rend.*, 118, 1282—1283).—Two litres of the insects, *Pyrrhocoris apterus*, were dried in a vacuum and treated with carbon bisulphide, which dissolves the fatty matter and also the colouring matter. The latter is also dissolved by light petroleum and by alcohol, and the solutions have an absorption spectrum similar to that of carotene. The solid colouring matter yields a greenish-blue coloration when mixed with concentrated sulphuric acid. It would seem, therefore, that the red pigment of *P. apterus* is very similar to carotene; it produces no appreciable physiological effect on guinea pigs or mice.

C. H. B.

Pyrazole. By L. KNORR (*Annalen*, 279, 188—232).—The author discusses at length the constitution of benzene and pyrazole; he considers that pyrazole is a tautomeric compound which in its derivatives has the following constitutions.



Further, in the case of the first formula, the double bonds may undergo rearrangement, so that the hydrogen atom combined with the one nitrogen atom becomes attached to the other; pyrazole thus behaves as a symmetrical molecule and the 3-methylpyrazole is identical with 5-methylpyrazole, just as 1 : 2 and 1 : 6 di-derivatives of benzene are identical, owing to oscillation of the double bonds in the Kekulé formula.

The author has prepared both 3- and 5-methylpyrazoles by a number of methods which are indicated below, and the identity of the products has been fully established.

3-Methylpyrazole may be prepared by Marchetti's method (*Abstr.*, 1893, i, 179), and by adding hydrazine sulphate and soda to a cooled

solution of sodioformylacetone; dimethylmethylen-hydrazine is also obtained in the latter process.

3 : 5-pyrazoledicarboxylic acid is obtained by the oxidation of 3 : 5-methylpyrazolecarboxylic acid, or of 3 : 5-dimethylpyrazole; it crystallises with $1\text{H}_2\text{O}$, and is identical with the acid melting at 289° , prepared by Buchner and Papendieck (Abstr., 1893, i, 431; compare Marchetti, *loc. cit.*). The *hydrogen potassium* salt is a characteristic one, it crystallises without water and is sparingly soluble.

Ethyl methylpyrazolecarboxylate is obtained by the condensation of ethyl acetoneoxalate with hydrazine; it crystallises in tables melting at $82-83^\circ$, and is readily hydrolysed.

1 : 3-Phenylmethylpyrazole (Claisen and Roosen, this vol., i, 346), yields methylpyrazole on oxidation with alkaline permanganate, and gives 1-nitrophenyl-3-methylpyrazole (paranitro?) on treatment with fuming nitric acid; this crystallises in long needles melting at 166° ; on reduction with stannous chloride, the nitro-derivative is converted into 1-amidophenyl-3-methylpyrazole, $\text{C}_{10}\text{H}_{11}\text{N}_3$, which crystallises in lustrous prisms and melts at 99° . On oxidation with potassium permanganate this substance and also 1-phenyl-5-methylpyrazole, or its amido-derivative, yields methylpyrazole.

1-Nitrophenyl-5 : 3-methylpyrazolecarboxylic acid, $\text{C}_{11}\text{H}_9\text{N}_3\text{O}_4$, obtained by nitrating phenylmethylpyrazolecarboxylic acid, is crystalline and melts at $122-124^\circ$. It loses carbonic anhydride at $165-170^\circ$, yielding 1-nitrophenyl-5-methylpyrazole, which crystallises in lustrous leaflets melting at 161° . The corresponding *amidopyrazole*, obtained by reduction with stannous chloride, crystallises in long prisms melting at $201-202^\circ$.

3-Methylpyrazole *platinic chloride*, $(\text{C}_4\text{H}_5\text{N}_2)_3\text{PtCl}_4$, is prepared by crystallising the platinochloride from dilute hydrochloric acid; it forms yellow needles melting and decomposing at 253° . *Argento-methylpyrazole*, $\text{C}_4\text{H}_5\text{N}_2\text{Ag}$, is obtained as a voluminous, white precipitate by the action of ammoniacal silver nitrate on the base. 3-Methylpyrazole *silver nitrate*, $(\text{C}_4\text{H}_5\text{N}_2)_3\text{AgNO}_3$, crystallises in laminæ melting at 121° . 3-Methylpyrazole *mercuric chloride*, $(\text{C}_4\text{H}_5\text{N}_2)_3\cdot 3\text{HgCl}_2$, crystallises in needles melting at $165-168^\circ$.

Bromo-3-methylpyrazole, obtained by direct bromination of methylpyrazole, melts at 67° . Its *hydrobromide*, $\text{C}_4\text{H}_5\text{N}_2\cdot\text{Br}\cdot\text{HBr}$, separates on adding bromine to an aqueous solution of methylpyrazole and crystallises in needles melting at 135° .

4-Nitro-3-methylpyrazole, $\text{C}_4\text{H}_5\text{N}_3\text{O}_2$, is obtained by heating methylpyrazole with a mixture of nitric and sulphuric acids; it crystallises in prisms melting at 134° , and distils at 325° under 748 mm. pressure. The *sodium* and *potassium* derivatives were prepared.

3-Methylpyrazolesulphonic acid, $\text{C}_4\text{H}_5\text{N}_2\cdot\text{HSO}_3$, is prepared by sulphonating the pyrazole; it is very soluble in water, and melts and decomposes at $257-258^\circ$. The *barium* salt is obtained in anhydrous, pearly leaflets.

On heating methylpyrazole with methylic iodide in ethereal solution at 120° , a powerfully odorous *base* of the composition $\text{C}_5\text{H}_7\text{Me}_2\text{N}_2$ is obtained; it boils at about 150° , and is possibly a mixture. Excess of methylic iodide reacts with methylpyrazole, yielding a *dimethyl-*

pyrazole methiodide, $C_3H_2Me_2N_2, MeI$; it crystallises in needles and decomposes at 252° . The corresponding *methylic platinumchloride*, $(C_3H_2Me_2N_2)_2, Me_2PtCl_2$, decomposes at 225° .

3-Methylpyrazole is oxidised to pyrazole-3-carboxylic acid by potassium permanganate; this acid crystallises in prisms, decomposes into pyrazole and carbonic anhydride at 210 – 214° , and is doubtless identical with the acid melting at 208 – 210° obtained by Buchner and Pappendieck (*loc. cit.*).
W. J. P.

Condensation of Methylhydrazine with β -Diketones. By L. KNORR (*Annalen*, 279, 232–236).—1 : 3 : 5-Trimethylpyrazole, $C_3N_2HMe_3$, may be prepared by the interaction of methylhydrazine with acetylacetone in aqueous solution or by the action of soda on the methiodide obtained by heating 3 : 5-dimethylpyrazole with methylic iodide. It crystallises in long needles, melts at 37° , and boils at 170° under 755 mm. pressure; its odour recalls that of iodoform, and its aqueous solution has a neutral reaction. The sparingly soluble *picrate* crystallises in prisms melting at 131 – 133° ; the *hydrochloride* is hygroscopic, and crystallises in needles melting at 94 – 96° . The *aurchloride* with $1H_2O$ is obtained in needles melting at 91 – 94° , whilst the *platinchloride* melts at 187 – 191° . No argento-derivative could be prepared, but a double salt with mercuric chloride was obtained; it crystallises in six-sided leaflets melting at 164 – 169° . 1 : 3 : 5-Trimethyl-4-nitropyrazole, prepared by direct nitration of the pyrazole, crystallises in needles melting at 56 – 57° .

1 : 3 : 4 : 5-Tetramethylpyrazole is obtained by the condensation of methylhydrazine with methylacetylacetone; it boils at 190 – 193° , solidifies in the ice-chest, and has a more unpleasant odour than 1 : 3 : 5-trimethylpyrazole.

1 : 5-Dimethylpyrazolone may be prepared by the condensation of methylhydrazine with ethylic acetoacetate; it melts at 106 – 109° , and boils at 205 – 210° under 210 mm. pressure.
W. J. P.

Condensation of Hydrazine with Methylacetylacetone. By B. OETTINGER (*Annalen*, 279, 244–246).—3 : 4 : 5-Trimethylpyrazole, $C_3HMe_3N_2$, is formed by the action of hydrazine hydrate on methylacetylacetone; it boils at 232 – 233° under 753 mm. pressure, and crystallises in six-sided leaflets melting at 137 – 138° . It is volatile in a current of steam and sublimes at 100° . The *hydrochloride* crystallises in minute needles, decomposes at about 265° , and, with mercuric chloride, gives a double salt, $C_3H_{10}N_2, 2HgCl_2$, melting at 193 – 196° . The *picrate* crystallises in needles melting at 237 – 239° , whilst the double salt with silver nitrate, $(C_3H_{10}N_2)_2, AgNO_3$, crystallises in needles melting at 221° ; the argento-derivative, $C_3H_5N_2, Ag$, was also prepared.

On heating the base with methylic iodide, 1 : 3 : 4 : 5-tetramethylpyrazole is obtained; its *methiodide*, $C_7H_{12}N_2, MeI$, crystallises in needles melting at 192° whilst its *methylic platinumchloride*,



melts and decomposes at 215 – 216° .

W. J. P.

Condensation of Hydrazine with Dimethylacetylacetone. By L. KNORR and B. OETTINGER (*Annalen*, 279, 247—248).—
 3 : 4 : 4 : 5-Tetramethylpyrazole, $\begin{matrix} \text{N:CMe} \\ \text{N:CMe} \end{matrix} > \text{CMe}_2$, is obtained by the action of hydrazine hydrate on dimethylacetylacetone; it boils at 242—243° under 740 mm. pressure, and melts at 50—55°. This substance is typical of the symmetrical tautomeric constitution assigned to pyrazole by Knorr (this vol., i, 544). W. J. P.

Condensation of Hydrazine with Benzoylacetone and Ethylic Benzoylacetate. By B. SJOLLEMA (*Annalen*, 279, 248—256).—
 —3 : 5-Methylphenylpyrazole, $\text{CH} < \begin{matrix} \text{CPh:N} \\ \text{CMe:NH} \end{matrix}$, may be prepared by the action of hydrazine hydrate on benzoylacetone; it crystallises in needles melting at 128°, and boils at 326—327° (cor.). The hydrochloride is obtained as a crystalline powder, melting at 205°; the platinochloride and the picrate crystallise in yellow needles. The acetyl-derivative forms needles melting at 43°, and is hydrolysed by heating with soda. The dibromide, $\text{C}_{10}\text{H}_9\text{N}_2\text{Br}_2$, is obtained by direct bromination, and crystallises in needles melting at 205°; when heated with water, it yields 3 : 5-phenylmethyl-4-bromopyrazole melting at 93°.

On heating the base with methylic iodide, a phenyldimethylpyrazole methiodide, $\text{C}_{11}\text{H}_{13}\text{N}_2\text{MeI}$, which melts at 190°, is obtained; the methochloride and the methylic platinochloride, $(\text{C}_{11}\text{H}_{13}\text{N}_2)_2\text{Me}_2\text{PtCl}_2$, crystallise in needles melting at 50° and 216° respectively. On oxidising 3 : 5-phenylmethylpyrazole with potassium permanganate, a phenylpyrazolecarboxylic acid, which melts and decomposes at 230—240°, is obtained.

Ethylic 3 : 5-phenylmethylpyrazole-4-carboxylate and 3-phenylpyrazolone result from the condensation of hydrazine hydrate with ethylic benzoylacetate. The free acid, which crystallises in needles, decomposes at 260—265°, and on distillation yields carbonic anhydride and 3 : 5-phenylmethylpyrazole. The silver and barium salts are both amorphous. The acid yields 5-phenylpyrazole-3 : 4-dicarboxylic acid on oxidation with permanganate; this melts and decomposes at 235°, and seems to be identical with the dicarboxylic acid prepared by Buchner and Fritsch (*Abstr.*, 1893, i, 281), since both acids give the same phenylpyrazole melting at 78° on distillation. The latter can only be 5-phenylpyrazole, and not 4-phenylpyrazole, as stated by these authors. Further, the substance melting at 228°, described by Buchner and Dessauer (*Abstr.*, 1893, i, 282) as 5-pyrazole, must be the 4-isomeride. 5-Phenylpyrazole picrate crystallises in needles, melting at 168°. W. J. P.

Condensation of Hydrazine with Acetylacetone, Ethylic Acetylacetate, and Ethylic Ethylideneacetoacetate. By G. D. ROSENGARTEN (*Annalen*, 279, 237—243).—3 : 5-Dimethylpyrazole is obtained in quantitative yield by the action of hydrazine hydrate on acetylacetone (Marchetti, *Abstr.*, 1893, i, 177); the

argento-derivative crystallises in long needles melting at 152°. On heating the pyrazole with methylic alcohol and methylic iodide at 100—110°, 1 : 3 : 5-*trimethylpyrazole methiodide* is obtained (compare preceding abstracts); it crystallises with 1CHCl₃. The *methylic platinochloride*, (C₆H₁₀N₂)₃.Me₃PtCl₃, crystallises in long needles, melting at 222°.

Ethylic ethylideneacetoacetate or ethylic acetylacetoacetate interacts with hydrazine hydrate, forming *ethylic 3 : 5-dimethylpyrazole-4-carboxylate*, 3-methylpyrazolone, and the substance of the composition C₈H₈N₂O₃, previously described by Knorr (Abstr., 1887, 601); the compound last named is also obtained by the action of hydrazine hydrate on ethylic acetoacetate. In the action between ethylic ethylideneacetoacetate and hydrazine hydrate, 4-*ethylidene-bis-3-methylpyrazolone* (?),

$$\text{NH} < \begin{array}{c} \text{N} = \text{CMe} \\ \text{CO} - \text{CH} - \text{CHMe} \cdot \text{CH} - \text{CO} \end{array} \begin{array}{c} \text{CMe} \cdot \text{N} \\ \text{CH} - \text{CO} \end{array} > \text{NH}$$
, is also obtained; it crystallises in prisms, and melts and decomposes at 255°.

Ethylic 3 : 5-dimethylpyrazole-4-carboxylate crystallises with 2H₂O, and then melts at 60°, but when anhydrous it melts at 96°. It sublimes on the water-bath, and is volatile in a current of steam. The corresponding *acid* crystallises in small needles or leaflets, and melts and decomposes at 290°. On distillation or heating with water at 200°, it yields dimethylpyrazole and carbonic anhydride, whilst on oxidation with alkaline permanganate, it gives 3 : 4 : 5-pyrazole-tricarboxylic acid.

W. J. P.

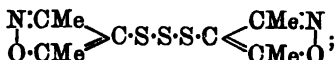
Action of Chloride of Sulphur on Acetylacetone. By A. ANGELI and MAGNANI (*Gazzetta*, 24, i, 342—370).—Sulphur dichloride and acetylacetone interact violently with formation of *thioacetylacetone*, CHAc₂S·CHAc₂; this crystallises in very beautiful, colourless, orthorhombic prisms melting at 67—72°; *a* : *b* : *c* = 0.9412 : 1.7239. Thioacetylacetone behaves like an acid, reddening litmus, decolorising phenolphthaleïn, and dissolving in soda, ammonia, or alkaline carbonates; it is precipitated from these solutions by hydrochloric acid, although slight decomposition occurs even in the cold, and becomes complete on boiling. Aqueous alcoholic solutions of the substance give precipitates with salts of copper or lead, but not with those of barium; with ferric chloride, a beautiful red colour is produced.

Thiodimethylisoxazole (?),
$$\begin{array}{c} \text{N} : \text{CMe} \\ \text{O} \cdot \text{CMe} \end{array} > \text{C} \cdot \text{S} \cdot \text{C} < \begin{array}{c} \text{CMe} \cdot \text{N} \\ \text{CMe} \cdot \text{O} \end{array}$$
, is obtained on boiling an alcoholic solution of thioacetylacetone with hydroxylamine hydrochloride; sulphurous anhydride is evolved, and the oxazole is ultimately obtained in colourless, lamellar crystals melting at 127—128°.

Thiodimethylphenylpyrazole,
$$\begin{array}{c} \text{NPh} \cdot \text{CMe} \\ \text{N} = \text{CMe} \end{array} > \text{C} \cdot \text{S} \cdot \text{C} < \begin{array}{c} \text{CMe} \cdot \text{NPh} \\ \text{CMe} \cdot \text{N} \end{array}$$
, is prepared by boiling thioacetylacetone with phenylhydrazine in acetic acid solution; it forms small, lustrous, colourless crystals melting at 114°.

Dithioacetylacetone (this vol., i. 209) also crystallises in the orthorhombic system; $a : b : c = 0.9317 : 1 : 1.6501$. Its aqueous alcoholic solution possesses a distinctly acid reaction, and gives precipitates with salts of copper or lead, but not with those of barium; it gives a red coloration with ferric chloride.

Trithioacetylacetone, $\text{CHAc}_2\text{S}_2\text{CHAc}$, is prepared by the action of sulphur monochloride on acetylacetone; the action is violent, and the product, after purification, is obtained in almost colourless, orthorhombic plates, melting at 130° ; $a : b : c = 0.7062 : 1 : 1.6797$. A very distinct morphotropic relationship exists between the crystals of these three thio-compounds. Trithioacetylacetone behaves as an acid, just as the mono- and di-thio-derivatives. On treatment with hydroxylamine hydrochloride, it yields trithiodimethylisoxazole,



this crystallises in beautiful, colourless needles, and melts at $65-66^\circ$. Trithioacetylacetone is converted into trithiodimethylphenylpyrazole, $\text{N}=\text{CMe} \begin{array}{c} \text{CMe}:\text{N} \\ | \\ \text{NPh}:\text{CMe} \end{array} \text{C} \cdot \text{S} \cdot \text{C} \begin{array}{c} \text{CMe}:\text{N} \\ | \\ \text{CMe}:\text{NPh} \end{array}$, by the action of phenylhydrazine; it is a crystalline powder, and melts at 141° .

W. J. P.

Pyrazine. By L. WOLFF (*Ber.*, 27, 2018—2019).—Attention is drawn to the discrepancy existing between the author's description of pyrazine (*Abstr.*, 1893, i, 373) and that of Stoehr (*loc. cit.*, 486). In support of his views, the author points out that not only do Stoehr's later results differ widely from those already given by that investigator, but that the specimen of pyrazine obtained by Gabriel and Pinkus from amido-aldehyde (*loc. cit.*, 734) agrees closely in melting point and boiling point with the base described by the author.

M. O. F.

Combination of Pyridine with Permanganates. By T. KLOBB (*Compt. rend.*, 118, 1271—1273).—Pyridine, like ammonia, forms crystalline compounds with silver, copper, cadmium, zinc, and nickel permanganates. They are more or less soluble in water, and very soluble in pyridine; when heated rapidly they explode, but when heated slowly, no explosion takes place. When moistened with sulphuric acid, or when suddenly compressed, they burn vigorously. Even at low temperatures they lose pyridine, and undergo partial oxidation; they should be prepared and dried at about 0° .

The silver compound, $\text{AgMnO}_4 \cdot 2\text{C}_5\text{NH}_5$, is obtained on adding a small quantity of pyridine to an aqueous solution of silver nitrate and potassium permanganate mixed in equivalent proportions. It is only very slightly soluble in water, and forms violet, microscopic crystals, which decompose at 65° . The other compound,



is obtained by pouring the mixed saline solutions into an excess of pyridine, or by gradually adding water to a 50 per cent. solution of silver permanganate in pyridine. It forms violet needles, which only explode at about 100° .

The copper salt, $\text{Cu}(\text{MnO}_4)_2 \cdot 4\text{C}_2\text{NH}_5$, is obtained in the same manner as the first silver salt, and forms beautiful, violet crystals, which decompose at 65° . The cadmium salt, $\text{Cd}(\text{MnO}_4)_2 \cdot 4\text{C}_2\text{NH}_5$, must be prepared from concentrated solutions at 0° , and forms tabular crystals, apparently rhombic; it decomposes at 65° . Both the zinc and nickel compounds are similar in composition, and are prepared in a similar manner. The nickel salt occurs as a violet, crystalline powder, or in nodules, and decomposes at 65° . Cobalt permanganate does not yield a similar compound.

C. H. B.

Additive Product of Pyridine and Chloracetone. By H. DRESER (*Arch. Pharm.*, 232, 183—186).—These two substances react to form a crystalline compound, $\text{C}_5\text{NH}_5\text{Cl} \cdot \text{CH}_3\text{COMe}$. The *mercuriochloride* of this substance crystallises in white needles, and melts at 119° (uncor.); the *picrate* melts at 141° (uncor.); the *platinochloride* melts and decomposes at $206\text{--}207^\circ$ (uncor.); and the *aurochloride* at $136\text{--}138^\circ$ (uncor.).

Quinoline did not yield an analogous product.

A. G. B.

Synthesis of Pyridine Derivatives from Aldehydes and Benzoylpiperidine. By L. RÜGHEIMER (*Annalen*, 280, 36—49).—The condensation of benzoylpiperidine with two molecular proportions of an aldehyde is accompanied by the elimination of the benzoyl group and 2 atoms of hydrogen; thus



Simultaneously 2 atoms of hydrogen migrate from the piperidine nucleus to the aldehydic groups, 3 : 5-disubstituted derivatives of pyridine being formed, whilst the liberated hydrogen reduces a portion of the aldehyde employed, with formation of the parent hydrocarbon.

3 : 5-Dibenzylpyridine, $\text{C}_5\text{NH}_3(\text{CH}_2\text{Ph})_2$, is obtained by heating 6 parts of benzaldehyde with 5 of benzoylpiperidine in a closed tube for six hours at $240\text{--}250^\circ$. The base is slightly soluble in water and readily in alcohol, crystallising from the latter in thin plates, which melt at 89° , the liquid boiling at 300° ; its basic character is but feeble, and the salts are decomposed by water. Dibenzylpyridine remains unchanged when heated at 125° with strong caustic soda, whilst dilute hydrochloric acid at 210° merely transforms it into the *hydrochloride*, melting at $164\cdot5\text{--}166^\circ$, and characterised by its low solubility in boiling benzene and the feathery aggregates in which it crystallises. On adding water to the alcoholic solution of this salt, the base is deposited as an oil, which soon solidifies. Strong hydrobromic acid at $175\text{--}180^\circ$ slightly alters the base, but at lower temperatures the *hydrobromide* alone is formed; this crystallises from hot benzene in thin tablets which melt at $148\cdot5^\circ$. The *nitrate* melts at $96\cdot5\text{--}98^\circ$. The *methiodide* was obtained in the form of an oil which yields an unstable molecular compound with chloroform, crystallising in plates. The *ethiodide* is deposited from alcohol in nodular aggregates of needles, and melts at 137° .

Tribenzylpyridine, $\text{C}_5\text{NH}_2(\text{CH}_2\text{Ph})_3$, which occurs as a bye-product

in the preparation of the dibenzyl-derivative, remains undissolved when the crude substance is treated with ether. It is with difficulty soluble in hot amyl alcohol, separating from this solvent in hexagonal plates which melt at 278—280°.

3:5-Dibenzoylpyridine, $C_6NH_5Bz_2$, is formed by the oxidation of 3:5-dibenzylpyridine; chromic acid is the agent employed, the base being scarcely attacked by potassium permanganate, even when heated with a strong solution of it. Dibenzoylpyridine forms long needles melting at 123°; it yields an *oxime*, and the *platinochloride* forms blunt, bright red needles. It possesses slightly basic properties, dissolving in dilute mineral acids when heated. M. O. F.

3-Benzoylpyridine-5-carboxylic acid, $COPh \cdot C_6NH_5 \cdot COOH$, and the Position of the Benzyl Group in Dibenzylpyridine. By L. RÜGHEIMER and W. KRONTHAL (*Annalen*, 208, 50—59).—This acid is the intermediate product in the oxidation of dibenzoylpyridine to dinicotinic acid. It separates from hot benzene in colourless needles, and melts at 199—201°; the *silver* and *copper* salts are well defined.

Paradinitro-3:5-dibenzylpyridine, prepared by adding the base in small quantities at a time to fuming nitric acid, forms yellowish needles which melt at 144—146°; its constitution is shown by the fact that the only nitrobenzoic acid formed on oxidation is the *para*-modification. It is sufficiently basic in character to form salts; the *nitrate* crystallises in colourless needles, and melts at 160—162°; the *hydrochloride* melts at 121—123°; the *platinochloride* melts at 225—226°. The *picrate*, which is almost insoluble in alcohol, melts at 175—177°; the *methiodide* at 190—193° and the *ethiodide* at 167—173°.

Paradiamido-3:5-dibenzylpyridine is obtained by reducing the dinitro-compound with stannous chloride and hydrochloric acid. It is insoluble in light petroleum, but dissolves in amyl alcohol, benzene, and alcohol, separating from the latter in needles which melt at 155—157°; the *hydrochloride* remains unfused at 250°. On oxidising diamidodibenzylpyridine with potassium permanganate, dinicotinic acid is formed; this result shows conclusively that the substituted pyridines obtained by the action of aldehydes on benzoylpyridine are 3:5-derivatives. M. O. F.

Cuminaldehyde and Benzoylpyridine (by L. RÜGHEIMER and W. HERZFELD, *Annalen*, 280, 60—73) and the **Isomeric Toluylaldehydes and Benzoylpyridine** (by L. RÜGHEIMER and K. DÖRING, *Annalen*, 280, 76—78).—When cuminaldehyde and benzoylpyridine are heated in a closed tube for eight hours at 235—240°, derivatives analogous to those described in the foregoing abstracts are obtained, accompanied by small quantities of cymene.

Paradisopropyl-3:5-dibenzylpyridine, $C_6NH_5(CH_2 \cdot C_6H_4 \cdot Pr^i)_2$, melts at 76—77°; it is feebly basic, the salts being decomposed by water. The *hydrochloride* melts at 182—183°. The *picrate*,



is soluble in alcohol, and melts at 111–113°. The *platinochloride* decomposes at 230–236°; the *aurochloride* forms deliquescent, yellow needles. The base yields crystalline *double salts* with mercuric chloride, cadmium chloride, and copper acetate, the latter forming bluish-violet crystals of the constitution $C_{25}H_{22}N, C_2H_3O_2, Cu(C_2H_3O_2)_2$. The *methiodide* is soluble in water, and melts at 173–174°; the *ethiodide* at 168–169°. The *methochloride* was obtained in crystalline scales which could not be recrystallised; the *platinochloride* of this salt melts at 216–219°. The oxidation of diisopropyldibenzylpyridine is carried out by means of chromic acid, 3:5-dibenzoylpyridine-*paradicarboxylic acid* being formed. This bibasic acid is insoluble in water, alcohol, and ether, but may be recrystallised from hot glacial acetic acid; it melts at 308°, decomposition and partial sublimation taking place simultaneously. The *ammonium* salt undergoes decomposition when its solution is evaporated, but the *calcium*, *copper*, and *silver* salts are well-defined. When the last-named is distilled alone in small quantities, 3:5-dibenzoylpyridine is formed (compare Koenigs, Abstr., 1892, 293).

Paratriisopropyltribenzylpyridine, $C_8NH_2(CH_2 \cdot C_6H_4Pr^i)_3$, is separated from the mixture of bases by means of its insolubility in ether; it melts at 299–302°. In addition to this compound, *para-isopropylbenzylpyridine* occurs as a bye-product in the preparation of the disubstituted compound; it was obtained as an oil, and its *platinochloride* forms rectangular plates which melt at 208–213°.

The derivatives obtained from the three isomeric tolyl aldehydes, in every way analogous to those already described, may be tabulated as follows.

	Diparaxylypyridine.	Dimetaxylypyridine.	Diortho-xylpyridine.
Base, $C_{21}H_{21}N$	m. p. 108·5°	m. p. 65–66·5°	m. p. 40·5°
Hydrochloride, $C_{21}H_{21}N, HCl$	180–182°	165–166°	191–104°
Platinochloride, $(C_{21}H_{21}N)_2, H_2PtCl_6$	252–255	185–186	171–174
Picrate, $C_{21}H_{21}N, C_6H_3(NO_2)_3 \cdot OH$	156–158	116–117	182–183
Methiodide, $C_{21}H_{21}N, MeI$	137°	105–107	152–153
Ethiodide, $C_{21}H_{21}N, EtI$	148–150	109–109·5°	148–142

The acid obtained by the oxidation of diparaxylypyridine is identical with that derived from paradiisopropyl-3:5-dibenzylpyridine. From dimetaxylypyridine, however, is obtained 3:5-dibenzoylpyridine-*metadicarboxylic acid*; this forms minute needles, which melt at 270–271°.

M. O. F.

Anderson's Pyridine Reaction. By A. COSSA (*Gazzetta*, 24, i, 393–397; compare Abstr., 1893, i, 364).—The term “Anderson's

reaction" is usually applied to the elimination of hydrogen chloride and formation of a platinopyridine chloride, $(C_5H_5N)_2PtCl_4$ (Anderson's platinic compound), which occurs on boiling an aqueous solution of a pyridine platinochloride $(C_5H_5N)_2H_2PtCl_4$. The author finds that a similar reaction occurs with the platinochlorides.

Pyridine platinochloride, $(C_5H_5N)_2H_2PtCl_4$, is deposited on strongly cooling a mixed solution of potassium platinochloride and pyridine hydrochloride; it crystallises in anhydrous monosymmetric prisms, and is very soluble in water, but insoluble in alcohol. On boiling its aqueous solution, or on heating the solid substance at 130° , platosemidipyrindine chloride, $(C_5H_5N)_3PtCl_4$ (Anderson's platinous compound), is deposited. If the boiling is not too prolonged, a double salt of the composition $(C_5H_5N)_2PtCl_4 \cdot (C_5H_5N)_3H_2PtCl_4$ is formed; it crystallises in long, yellow prisms. Both the platinochloride and the platinochloride also decompose slowly in aqueous solutions at the ordinary temperatures, giving Anderson's platinous and platinic compounds respectively.

The platinous compound is converted into the platinic compound by digesting it with nitro-hydrochloric acid at 100° . Anderson's statement that platopyridine chloride is obtained by treating platosemidipyrindine chloride with pyridine is inexact; a diplatinous compound seems to be formed. W. J. P.

Synthesis of Quinoline. By V. KULISCH (*Monatsh.*, 15, 276—279).—Quinoline is obtained by adding an aqueous solution of sodium hydroxide (1 : 2) to a solution of glyoxal in an excess of orthotoluidine, and heating the mixture in a reflux apparatus at 150° for $1\frac{1}{2}$ hours. The yield amounts to 35—40 per cent. of that required by theory. Other dehydrating agents, such as concentrated sulphuric acid and zinc chloride, give extremely bad yields.

The author is engaged in an examination of products of condensation of α -diketones and α -ketonic acids with orthotoluidine with the object of obtaining derivatives of quinoline. E. C. R.

Synthesis of Isoquinoline. By E. BAMBERGER and C. GOLDSCHMIDT (*Ber.*, 27, 1954—1957).—Isoquinoline is obtained when syn-cinnamaldoxime is heated with phosphoric anhydride at 60 — 70° . Anti-cinnamaldoxime, which is also obtained in the preparation of cinnamaldoxime, likewise yields isoquinoline under the same conditions.

A very small quantity of quinoline is obtained on heating cinnamaldehyde hydrazone with acetic anhydride at 215 — 225° , and also by passing dry hydrogen chloride through the melted hydrazone; in the latter process, a small quantity of a bye-product is also obtained, which melts at 135° , and is apparently a hydrazone. E. C. R.

Synthesis of Isoquinoline and its Derivatives. By C. POMERANZ (*Monatsh.*, 15, 299—306; *Abstr.*, 1893, i, 607).—The author has continued his researches on the production of isoquinoline from benzaldehyde and amidoacetal, and has obtained a yield equal to 50 per cent. of that required by theory. Benzylideneamidoacetal

is mixed with well-cooled, concentrated sulphuric acid (3 parts), and the mixture gradually added to 3 parts of sulphuric acid heated at 160°. Other condensation agents which the author employed gave very bad results.

α-Methylisoquinoline is obtained in a similar way from acetophenone and amidoacetal; but the yield only amounts to 15 per cent. of that required by theory. The product, which is isomeric with *γ*-methylisoquinoline obtained from methylbromophthalimide, is a colourless liquid, boils at 248° (uncor.), and has an odour between that of pyridine and quinoline. The *platinochloride* crystallises in bright red prisms with 4H₂O, and, when anhydrous, melts and froths up at 210°. The *sulphate* crystallises in flat, colourless prisms, and melts at 246—247°. The *dichromate* crystallises in yellowish-red prisms, and decomposes at 145.
E. C. R.

2:4-Dibromoquinoline. By A. CLAUS and A. AMMELBURG (*J. pr. Chem.*, [2], 50, 29—37).—2:4-Dibromoquinoline melts at 112°, not 110° (Abstr., 1890, 172). The *methiodide* melts at 287°; the *methochloride* becomes discoloured at 145° and melts at 236°, whilst its *platinochloride* decomposes and melts at 249°. The *hydrobromide* of 2:4-dibromoquinoline melts at 288°; its *perbromide*, C₈NH₂Br₃·HBr·Br₂, obtained by brominating the hydrobromide in ether, forms orange tables, melting at 215°. By heating the perbromide with bromine at 200°, 2:4:4'-tribromoquinoline is obtained as the chief product; this crystallises in colourless needles and melts at 125—126°; a more highly brominated compound (colourless needles, m. p. 148°) is formed at the same time. The *platinochloride* of 2:4:4'-tribromoquinoline was prepared, but the base is too feeble to form a methiodide.

1:2:4-Nitrodibromoquinoline is the sole product of the nitration of 2:4-dibromoquinoline; it crystallises in short, colourless prisms and plates, and melts at 198°; the *platinochloride* becomes dark at 220°, melting at 291°. By reduction, the nitro-derivative easily passes into 1:2:4-amidodibromoquinoline, which crystallises in colourless needles and melts at 127°; the *hydrochloride* melts at 191°; the *platinochloride* is also described.

1:2:4-Tribromoquinoline, obtained from the above amido-derivative through the diazo-reaction, crystallises in colourless, lustrous needles, melts at 141°, and sublimes; no methiodide could be obtained, but the *platinochloride* was prepared, and was found to melt and decompose at 280°. A discussion as to the orientation of this tribromoquinoline concludes the paper.
A. G. B.

Condensation Products of Ortho- and Para-hydroxybenzaldehyde with Quinaldine. By S. DZIERZGOWSKI (*Ber.*, 27, 1979—1983).—Salicyl ethylenequinoline has been previously obtained by Wallach and Wüsten (*Ber.*, 16, 2007) from quinaldine and ortho-hydroxybenzaldehyde; it is insoluble in alkali carbonates, dissolves in acids with an orange colour, does not reduce copper or silver solutions, and gives no coloration in alcoholic solution with ferric chloride. The *hydrochloride* crystallises in orange-red needles with 1 or 1½H₂O

according to circumstances, melts and decomposes at 255—260°, and undergoes dissociation on prolonged boiling with water. The salt gives a series of yellow, amorphous precipitates with the ordinary alkaloïd reagents. The *sulphate*, *acetate*, *oxalate*, and *tartarate* are crystalline and sparingly soluble. *Salicylethyltetrahydroquinoline*, $C_{17}H_{19}NO$, is prepared by the reduction of the quinoline by means of sodium, and crystallises in colourless, slender needles, melting at 121°. The base reduces silver, but not copper, solutions, dissolves in concentrated sulphuric acid without coloration, and is oxidised to a red dye by nitric acid. The *hydrochloride* crystallises in prismatic plates, melts at 223—225°, gives, with ferric chloride, a yellowish coloration, changing to brown; phosphomolybdic acid and phosphotungstic acid produce white, amorphous precipitates, potassium bismuthiodide, mercuriodide, and cadmioidide give yellow precipitates.

Parahydroxybenzethylenequinoline gives no coloration with ferric chloride. Cryoscopic molecular weight determinations in phenol agree with the formula $C_{17}H_{19}NO$. The *hydrochloride* crystallises with $1\frac{1}{2}H_2O$ in purple-reddish needles, and melts and decomposes at 264—266°. *Parahydroxyethyltetrahydroquinoline* is prepared in a similar manner to the ortho-derivative; it crystallises in colourless rhombohedra melting at 115°, and reduces silver solutions on boiling. The *hydrochloride* crystallises in colourless needles, and melts at 282°; with ferric chloride, it gives an olive-brown coloration, changing to purple-red, and white precipitates with phosphotungstic and phosphomolybdic acids. Ortho- and para-benzethylenequinoline readily combine with bromine to form compounds, which are being further investigated.

J. B. T.

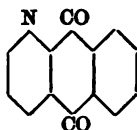
Anthrapyridinequinones. By A. PHILIPS (*Ber.*, 27, 1923—1927).—Bernthsen and Mettegang have shown (*Abstr.*, 1887, 737) that quinolinic anhydride is converted into 3-benzoylpicolinic acid by the action of benzene and aluminium chloride, but they were unable to bring about the condensation of the acid into an anthrapyridinequinone analogous to the conversion of orthobenzoylbenzoic acid into anthraquinone. The author has carried out a similar series of reactions with an isomeride of quinolinic acid, namely, cinchomeronic acid, and has succeeded in obtaining β -anthrapyridinequinone in quantity.

When cinchomeronic anhydride is heated with benzene and aluminium chloride, it is converted into 4-benzoylnicotinic acid,

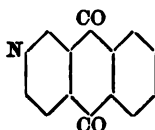


which forms a yellowish, crystalline mass, melts at 216°, and sublimes partly undecomposed; at 260°, however, it evolves carbonic anhydride, and is converted into a *phenyl pyridyl ketone*, $C_6NH_4\cdot COPh$; this is isomeric with the ketone obtained from 3-benzoylpicolinic acid by Bernthsen and Mettegang, so that the new ketone, and the acid from which it is obtained, must contain the benzoyl group in the 4-position. To convert the acid into *anthrapyridylquinone*, it is heated with concentrated sulphuric acid at 175°, and the brown solution after being poured into water, is neutralised with ammonia. The precipitated quinone, when recrystallised from carbon tetrachloride, forms needles,

melting at 170°, and subliming, on careful heating, in long needles, resembling those of anthraquinone. It dissolves in dilute acids, and, on treatment with zinc dust and aqueous soda, gives a wine-red solution. Two isomeric anthrapyridinequinones are possible, namely,



α -Anthrapyridylquinone.



β -Anthrapyridylquinone.

As the above ketone is formed from a 4-benzoyl-compound, it must be the β -derivative.

The β -derivatives being so readily obtained, the author has repeated Bernthsen and Mettegang's experiments with 3-benzoylpicolinic acid. The results obtained show that, contrary to the statement of these investigators, α -anthrapyridylquinone is, in reality, obtained on heating the 3-benzoyl compound with sulphuric acid at 270°; the yield is, however, extremely small. It crystallises in needles, melts at 280°, and sublimes in flat needles of a pure yellow colour. With zinc dust and aqueous soda, it forms a dark blue solution. H. G. C.

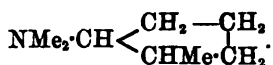
Constitution of Dimethylpiperidine and its Homologues.

By A. LADENBURG, M. MUGDAN, and O. BRZOSTOVICZ (*Annalen*, 279, 344—366).—Dimethylpiperidine (Hofmann, Abstr., 1888, 813), when treated with hydrogen chloride at 220°, is converted into dimethyl-

pyrrolidine, $\text{CH}_3\text{CH}(\text{NMe})\text{CH}_2\text{CH}_2\text{CH}_3$. If the trimethylpyrrolidinium hydroxide, prepared from this base by the action of methylic iodide and silver oxide, is distilled, it decomposes into water and the original dimethylpiperidine. Dimethylpyrrolidine hydrochloride, moreover, loses methylic chloride when heated in a stream of hydrogen chloride, methylpyrrolidine being formed. The platinochloride of this compound melts at 172—173°, the *aurochloride* at 212°. This behaviour is in agreement with the results previously obtained by Merling (Abstr., 1891, 1506), and confirms the formula $\text{CH}_3\text{CH}(\text{NMe})\text{CH}_2\text{CH}_2\text{CH}_3$, which has been given to dimethylpiperidine.

Dimethylconiine, when treated in a similar manner, behaves differently, and is converted into coniine. Dimethylconiine itself is strongly dextrorotatory, $[\alpha]_D = +17.04$, and, therefore, should contain an asymmetric carbon atom. The formula $\text{CH}_3\text{CH}(\text{NMe})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, which expresses its relation to dimethylpiperidine, does not fulfil this condition, whilst the alternative formula $\text{CH}_3\text{CH}(\text{NMe})\text{CH}_2\text{CH}_2\text{CH}(\text{NMe})\text{CH}_2\text{CH}_3$ fails to express the different behaviour towards hydrogen chloride. The only formula which satisfies both of these conditions is the following, $\text{NMe}_2\text{CH}(\text{CH}_2)_4\text{CH}_3$.

Dimethyl- α -pipecoline, like coniine, is not converted by hydrogen chloride into a pyrrolidine derivative, but yields methyl- α -pipecoline. From analogy with dimethylconiine, therefore, the formula of dimethylpipecoline should be



The authors have now found that dimethylpipercoline is optically active, although only to a very slight degree, and this is in accordance with this formula, which contains an asymmetric carbon atom. The analogy between dimethylpiperidine and dimethylconiine is, however, not brought out by the new formula for the latter, although the two bases are in many respects very similar. Thus dimethylconiine, like dimethylpiperidine, unites with 2 atoms of iodine to produce a *diiodide*, $\text{C}_{10}\text{H}_{21}\text{NI}_2$, which forms white crystals melting at 184° , and, on treatment with silver chloride, forms a *chloriodide*, $\text{C}_{10}\text{H}_{21}\text{NClI}$, the *platinochloride* of which can be obtained in the crystalline form. The new formula, moreover, does not explain the ease with which the hydrochlorides of dimethylconiine and dimethylpipercoline unite with 1 mol. of hydrogen chloride. A. H.

Piperidylacetal. By 'R. STOERMER and O. BURKEET (*Ber.*, 27, 2016—2018).—*Piperidylacetal*, $\text{C}_6\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, is formed when monochloroacetal is heated with piperidine (2 mols.) until piperidine hydrochloride no longer separates. The pure base boils at $219\text{--}221^\circ$ (uncorr.); the *hydrochloride* is deliquescent, the *platinochloride* crystallises in orange needles, which melt at 134° , and the *aurochloride* melts at 96° . The *methiodide* and *ethiodide* melt at 119° and 123° respectively, and additive compounds have been also obtained with propylic bromide, allylic iodide, and monochloroacetone. A cold silver solution is quickly attacked by the base, which also slightly reduces Fehling's solution when heated. M. O. F.

Sulphonepiperidide and its Oxidation Product Sulphone- δ -Amidovaleric acid. By A. TÖHL and F. FRAMM (*Ber.*, 27, 2012—2016).—Sulphuryl chloride reacts with piperidine as with secondary amines, forming *sulphonepiperidide*, $\text{SO}_2(\text{NC}_5\text{H}_{10})_2$, which crystallises from dilute alcohol in large, lustrous plates, melts at 93° , and boils at 230° . It is not affected by boiling with soda or concentrated hydrochloric acid, but at 200° is resolved by the latter into sulphuric acid and piperidine. The yield is about 50 per cent. of the theoretical. The *tetrabromo-derivative* is deposited from glacial acetic acid in lustrous crystals, melting and decomposing at $203\text{--}204^\circ$. By the action of chlorine in excess on sulphopiperidide in glacial acetic acid, *tetrachlorosulphonepiperidone*, $\text{SO}_2[\text{N} < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} \cdot \text{CHCl} \end{array} > \text{CHCl}]_2$, is formed; it crystallises from dilute alcohol in colourless plates, melts at 158° and is being further investigated. *Sulphone- δ -amidovaleric acid* $\text{SO}_2(\text{NH}\cdot[\text{CH}_2]_4\cdot\text{COOH})_2$, prepared by the oxidation of sulphonepiperidide with potassium permanganate, crystallises in small, colourless plates, and melts at 165° . The yield is 60 per cent. of the theoretical. The acid is hydrolysed by the action of water at 160° , and of hydrochloric acid at 100° . The *barium salt* melts at 246° , and, like the *copper salt*, which melts at 232° , is pulverulent; the *lead salt* crystallises in large, lustrous plates, melting at 198° . All these salts con-

tain $\frac{1}{2}$ H₂O. The *methylic* and *ethylic salts* crystallise in large, lustrous plates melting at 81–82° and 69° respectively. The *anhydride* (*sulphonepiperidone*), $\text{SO}_2[\text{N} \langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \rangle \text{CH}_2]_2$, crystallises from ether in highly refractive prisms melting at 141°. J. B. T.

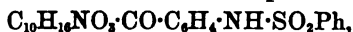
Technical Preparation of Cocaine from Associated Alkaloids. By C. LIEBERMANN (*Ber.*, 27, 2051–2053).—The author anticipates a misconception to which the recent publication of Einhorn and Willstätter under this title (this vol., i, 478) might give rise. M. O. F.

Substitution Derivatives of Cocaine. By A. EINHORN and H. HIS (*Ber.*, 27, 1874–1879).—Derivatives of cocaine, in which the substitution is in the benzoyl-group, may be prepared from ecgonine by converting it into the ether, and then acting on the latter with the anhydride or chloride of a substituted benzoic acid.

Orthochlorococaine, $\text{C}_{10}\text{H}_{11}\text{NO}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Cl}$, forms small, white crystals melting at 63–64°. The *platinochloride* crystallises in orange-coloured plates, and the *aurochloride*, in thin, yellow plates. The *hydriodide* crystallises from dilute alcohol in transparent lamellæ melting at 196–197°. *Orthochloro-d-cocaine* is prepared from d-ecgonine, and forms compact white crystals. The *hydrochloride* which crystallises in thin, prismatic plates, melts and decomposes at 208°. The *platinochloride* melts at 210–211°, and the *aurochloride* at 152°. *Metanitrococaine*, $\text{C}_{10}\text{H}_{11}\text{NO}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{NO}_2$, is obtained by the direct nitration of cocaine, and crystallises from alcohol in large, colourless prisms melting at 76–77°; when boiled with hydrochloric acid, it yields metanitrobenzoic acid. The *hydrochloride* forms prismatic needles; the *nitrate* melts at 164°; the *platinochloride* at 237°; and the *aurochloride* at 207.5–208°. *Metamidococaine* is formed when the nitro-compound is reduced with tin and hydrochloric acid; it crystallises from alcohol in colourless, compact crystals, and melts at 125°. The *dihydrochloride* forms transparent, prismatic tablets, and melts at 227–228°, whilst the *dihydriodide* is a yellowish powder, and melts at 219°. *Metacocaine-urethane*, $\text{C}_{10}\text{H}_{11}\text{NO}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{COOEt}$, is obtained by the action of ethylic chlorocarbonate on amidococaine. It crystallises from dilute alcohol in compact crystals melting at 143°. The *hydrochloride* is remarkably hygroscopic. *Metahydroxycocaine*, which is prepared by diazotising a solution of amidococaine hydrochloride, and boiling the liquid, crystallises from benzene in plates melting at 123°; it is soluble in aqueous soda, and is reprecipitated by carbonic anhydride. The *hydrochloride* forms dull, white, indistinct crystals; the *platinochloride* crystallises in well-developed, prismatic plates, and the *aurochloride* melts at 181–182°. A. H.

Substitution Derivatives of d-Cocaine. By A. EINHORN and E. S. FAUST (*Ber.*, 27, 1880–1887; compare foregoing Abstr.).—*Metanitro-d-cocaine*, obtained by the direct nitration of d-cocaine, is a colourless syrup. The *hydrochloride*, *hydrobromide*, *hydriodide*, and *nitrate* are all crystalline; the *platinochloride* melts at 232°; and the *aurochloride* at 168°. *Metamido-d-cocaine* crystallises

from dilute alcohol in large, colourless, tetrahedral crystals, or in slender needles, and melts at 116—117°. The *dihydrochloride* melts at 208—209°, whilst the *aurochloride* melts and decomposes at 98°. *Metamido-d-cocaine methiodide* melts at 197—198°. *Acetylamido-d-cocaine* is obtained by the action of acetic chloride on the amido-compound; it forms small plates, and melts at 44—45°. The *hydrochloride* forms small plates, and melts at 196—197°. *Benzoylamido-d-cocaine* is a colourless syrup, but yields a crystalline *hydrochloride*, which melts at 216—217°. *Metabenzenesulphonamido-d-cocaine*,



crystallises from dilute alcohol in small, yellowish plates, which melt at 69°.

d-Cocaine-urethane is obtained as a colourless oil, which crystallises with great difficulty, forming prismatic needles melting at 100—101°. The *hydrochloride* melts at 214°. *d-Cocainecarbamide* is obtained by the action of potassium cyanate on the amido-compound, and forms small, scale-like crystals melting at 72°. The *hydrochloride* melts at 135°. *d-Cocainephénylthiocarbamide*, $\text{C}_{10}\text{H}_{16}\text{NO}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, is obtained by the direct union of the amido-compound with phenylthiocarbimide; it forms microscopic crystals, and melts at 190—193°. *d-Cocainethiocarbamide*, $(\text{C}_{10}\text{H}_{16}\text{NO}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH})_2\text{CS}$, is obtained by the action of carbon bisulphide on *d-cocaine* as a fine, yellow powder, which melts at 63°. *Metahydroxy-d-cocaine* crystallises from dilute alcohol in radially grouped prisms melting at 82°. The *hydrochloride* melts and decomposes at 201°. *d-Cocaineazodimethylaniline*, prepared by adding dimethylaniline to a solution of diazo-*d-cocaine* hydrochloride, crystallises from alcohol in brick-red plates, and melts at 220°. The *hydrochloride* forms a deep, bluish-violet coloured solution in water. *d-Cocaineazodiphenylamine*, prepared in a similar manner, forms dark red plates melting at 172—173°. *d-Cocaineazoa-naphthylamine* forms red flakes, and could not be obtained in the crystalline stato.

A. H.

Cytisine and Ulexine. By A. PARTHEIL (*Arch. Pharm.*, 232, 161—177; compare *Abstr.*, 1893, i, 119).—Attempts to invert cytisine failed. The crystallographical measurements of the nitrate, hydrobromide, and *d-tartrate*, $\text{C}_{11}\text{H}_{14}\text{N}_3\text{O}(\text{CHOH}\cdot\text{COOH})_2 + 2\text{H}_2\text{O}$, prepared from cytisine and from ulexine respectively, confirm the identity of the two bases. These measurements, as well as those of cytisine hydriodide and methylcytisine platinochloride, are given in the paper.

The author has already shown that the apparent difference between the behaviour of cytisine and ulexine towards bromine, as interpreted by Magalhaes (*Abstr.*, 1891, 750) and by Gerrard and Symons (*Abstr.*, 1890, 180; 1891, 334), is due to a misinterpretation of the latter chemists' analytical data. When bromine (50 grams) is added to an alcoholic solution of cytisine (5 grams), the precipitate which is at first formed redissolves, and an orange-yellow microcrystalline powder then separates. This is a *perbromide* of the formula



When this is digested with alcohol, the hydrobromide,



is obtained in colourless, silky needles which melt at 223° . By decomposing this hydrobromide with sodium hydroxide, *dibromocytisine*, $\text{C}_{11}\text{H}_{13}\text{Br}_2\text{N}_2\text{O} + 3\text{H}_2\text{O}$, is precipitated in gelatinous flocks. The boiling aqueous solution of the base becomes gelatinous as it cools. Ulexine behaves similarly towards bromine. *Dibromocytisine nitrate*, $\text{C}_{11}\text{H}_{13}\text{Br}_2\text{N}_2\text{O} \cdot \text{HNO}_3$, prepared from the hydrobromide by means of silver nitrate, melts and decomposes at 196 – 197° . The *acetyl-derivative*, $\text{C}_{11}\text{H}_{11}\text{AcN}_2\text{Br}_2\text{O}$, crystallises in greenish-yellow needles melting at 164° . *Dibromocytisine platinochloride* and *aurochloride* are described.

Baryta water and moist silver oxide have no action on dibromocytisine; alcoholic potash in a sealed tube at 160 – 170° removes bromine from it, but the investigation of the action is not completed. Phosphorus pentachloride does not attack cytisine in chloroform solution.

By treating cytisine nitrate with fuming nitric acid, a *nitronitroso-cytisine*, $\text{NO} \cdot \text{C}_{11}\text{H}_{13}\text{N}_2\text{O} \cdot \text{NO}_2$, is obtained in yellow crystals; it is soluble in boiling water and melts at 237° .

A. G. B.

Ptomaine from Urine in a Case of Cancer. By A. B. GRIFFITHS (*Compt. rend.*, 118, 1350–1351).—The urine of a patient suffering from cancer (*cancer uteri*) contained a ptomaine *cancerine* of the composition $\text{C}_8\text{H}_8\text{N}_2\text{O}_5$. It crystallises in white microscopic needles, which dissolve in water and have an alkaline reaction. It forms a hydrochloride, platinochloride, and aurochloride, and gives a yellow precipitate with phosphotungstic acid, a brownish precipitate with phosphomolybdic acid, a red with silver nitrate, grey with mercuric chloride, and brownish precipitate with Nessler's reagent. It is very poisonous, and produces fever, and death in three hours.

C. H. B.

Peptone Salts of Egg-Albumin. By C. PAAL (*Ber.*, 27, 1827–1851; compare *Abstr.*, 1892, 895).—A number of peptone hydrochlorides have been prepared by the action of hydrochloric acid on egg-albumin under varying conditions of concentration, temperature, &c., fully described by the author. These salts are colourless, or pale-yellow, brittle, and amorphous, and are almost as hygroscopic as phosphoric anhydride; the latter property increases with the amount of combined acid. They are miscible with water in all proportions, dissolve readily in glacial acetic acid, more sparingly in phenol, and their solubility in the alcohols varies inversely with the molecular weight of the solvent, resembling the corresponding salts of the glutin-peptones in this respect. These compounds are not altered at 130° , have a sour, cheesy flavour, with a bitter aftertaste; they give the biuret, xanthoprotein, and Millon's reactions, are incompletely precipitated from aqueous solution by phosphotungstic acid, and, in contrast to the glutin-peptone salts, yield soluble double salts with mercuric chloride. That they are true peptones is shown by the fact that little or no precipitate is produced with ammonium sulphate

or sodium chloride, and the subsequent addition of an acid or alkali causes no change. Although the salts in aqueous solution redden litmus paper, no free acid is present, as repeated evaporation of the liquid causes no change in the composition of the peptone. The chlorine is only partially removed by the addition of silver nitrate. Certain of the salts were found to yield small quantities of methyl- and ethyl-derivatives by treatment with the respective alcohols. In the salts of the albumin-peptones, as in those of the gluten-peptones, the quantity of acid present is in inverse proportion to the molecular weight.

The *free peptones* are prepared from the hydrochlorides by the action of silver sulphate in the manner previously described (*loc. cit.*); the yield is 70—80 per cent. of the theoretical. They give the usual peptone reactions, are less hygroscopic than the salts, are sparingly soluble in methylic alcohol, and almost insoluble in ethylic alcohol. The *barium salts* are colourless and pulverulent, readily soluble in water, and somewhat hygroscopic. Zinc and copper salts produce no precipitate in solutions of the barium salt; with ferrous sulphate, *ferrous peptonate* is obtained in solution, and gradually decomposes in presence of air into ferric hydroxide and peptone. *Silver peptonate* and *lead peptonate* are yellow, flocculent, insoluble precipitates, stable towards light. *Mercuric peptonate* is colourless, amorphous, and insoluble. Two *lead peptone sulphates* were also obtained; they are somewhat hygroscopic; the aqueous solution is pale, yellowish-brown, and is not decomposed by boiling.

Gastric juice converts albumin into peptones, and, as with hydrochloric acid, half the product consists of soluble (Hemi) peptones, half of insoluble (Anti) peptones; these were further separated by dialysis, and in their general properties they resemble those described above.

A sample of commercial "albumin peptone" was found to consist almost entirely of albumoses, one of which is probably identical with Schrötter's alcohol soluble albumose.

Molecular weight determinations of the peptone salts and peptones by the cryoscopic and boiling point methods show that, exactly as in the case of the gluten derivatives, the percentage of acid increases as the molecular weight becomes smaller, and, as the molecular weights indicated by the first method were only half those deduced from the second, it follows that in the albumin-peptones also, one molecule of peptone is combined with one of hydrochloric acid. The molecular weight of the free peptones is about 400. The author concludes that the hydrolysis of the proteïds (peptonisation) can be followed, step by step, by the increasing proportions of acid, combined with the products characteristic of each phase of the reaction.

J. B. T.

Organic Chemistry.

Tautomerism. By J. W. BRÜHL (*Ber.*, **27**, 2378—2398, and *J. pr. Chem.* [2], **50**, 119—221).—See this vol., ii, 433.

Preparation of Bromoform. By P. FROMM (*Chem. Centr.*, 1894, i, 671—672; from *Pharm. Zeit.*, **39**, 164).—When calcium hypochlorite (3 mols.) and potassium bromide (6 mols.) are allowed to react with acetone (2 mols.), and the product distilled with steam, the yield of bromoform is only one-third of the theoretical, for the calcium hydroxide formed in the reaction decomposes some of the bromoform, forming calcium bromide, water, and carbonic oxide. The theoretical yield can be nearly attained by allowing the mixture to cool to 50°, adding an equal amount of calcium hypochlorite, and $\frac{3}{4}$ part of acetone, distilling with steam, and adding three times, at intervals, $\frac{1}{2}$ part acetone.

If for 1 mol. of acetone, 6 mols. of calcium hypochlorite, and 6 mols. of potassium bromide are taken, carbon tetrabromide is obtained in amount equal to 40—45 per cent. of the theoretical. C. F. B.

Bromine Derivatives of Tetrachlorethylene. By A. BESSON (*Compt. rend.*, **119**, 87—90).—When tetrachlorethylene is mixed with aluminium bromide in presence of an inert gas, and is gently heated, several bromochlorethylenes are obtained, and can be separated by distillation under low pressure.

Bromotrichlorethylene, C_2Cl_3Br , melts at -12° to -13° , and boils at $145-148^\circ$; sp. gr. at $15^\circ = 2.02$. It is not attacked by bromine in the dark even at 100° , but in sunlight complete combination takes place with formation of $C_2Cl_4Br_2$, a white compound which sublimates at $100-125^\circ$ under low pressure, and condenses in small prismatic crystals which melt and partially decompose at $178-180^\circ$; sp. gr. at $18^\circ = 2.44$.

Dibromodichlorethylene, $C_2Cl_2Br_2$, melts at $1-2^\circ$, and boils at $169-171^\circ$; sp. gr. at $15^\circ = 2.35$. Bourgoin has previously obtained a compound of the same composition by the action of aniline on $C_2Cl_4Br_2$ at 100° , and it is possible that the two compounds are isomeric, and have the constitutions $CCl_2.CBr_2$ and $CClBr.CClBr$ respectively. The compound $C_2Cl_2Br_2$ combines slowly with bromine under the influence of light, and yields a white solid, $C_2Cl_2Br_4$, which sublimates under low pressure at about 150° , and melts at $194-195^\circ$. Another compound, C_2Cl_3Br , melting at about 180° , has been described, and it is possible that the two are isomeric.

Ozonised oxygen combines slowly with dibromodichlorethylene, with formation of some carbonic chloride and liberation of bromine, which forms $C_2Cl_4Br_4$. The liquid has a disagreeable odour, and fumes on exposure to air; the fraction boiling at about 150° contains the compound $CClBr_2.COCl$, which yields the acid $CClBr_2.COOH$ when treated with water.

The product of the action of aluminium bromide on tetrachloroethylene also contains the compound C_2ClBr_3 , already described by Demole.

C. H. B.

Tribromacetoneitrile. Some Derivatives of Polymeric Trichloracetoneitrile. By C. BROCHE (*J. pr. Chem.* [2], 50, 97—118; compare *Abstr.*, 1893, i, 289).—Tribromacetamide is best made by carefully introducing aqueous ammonia under a layer of ethylic tribromacetate, and allowing the whole to remain for 12 hours at a temperature below 0° . Ethylic tribromacetate can be conveniently prepared by saturating an absolute alcoholic solution of tribromoacetic acid with dry hydrogen chloride, the solution being cooled with ice and kept cool for 12 hours after complete saturation.

When concentrated aqueous ammonia is introduced under a layer of an ethereal solution of polymeric tribromacetoneitrile, *diamidoperbromomethylcyanidine*, $CBBr_3 \cdot C_3N_3(NH_2)_2$, is obtained; this forms white crystals, and does not melt below 300° . If the polymeric nitrile is shaken with dry ammonia gas in a flask that has been heated on the water bath, *amidodiperbromomethylcyanidine*, $C_3N_3(CBr_3)_2 \cdot NH_2$, is obtained; it forms white crystals, and melts and decomposes at 184 — 185° . When aqueous methylamine is introduced beneath an ethereal solution of the polymeric nitrile, *methylamidodiperbromomethylcyanidine*, $C_3N_3(CBr_3)_2 \cdot NHMe$, is formed; it melts at 192° . If an absolute alcoholic solution of the polymeric nitrile is heated on the water bath with excess of methylamine, then white *dimethyldiamidoperbromomethylcyanidine*, $CBBr_3 \cdot C_3N_3(NHMe)_2$, melting at 263 — 264° , is formed. When aniline is introduced beneath a layer of an ethereal solution of the polymeric nitrile, yellow *anilinediperbromomethylcyanidine*, $C_3N_3(CBr_3)_2 \cdot NHPh$, melting at 205° , is obtained, whereas an alcoholic solution of the polymeric nitrile if heated with excess of aniline on the water bath, yields violet *dianilinediperbromomethylcyanidine*, $CBBr_3 \cdot C_3N_3(NHPh)_2$, melting at 280° . Polymeric trichloroacetoneitrile does not yield a derivative with aniline, nor does amidodiperchloromethylcyanidine, $NH_2 \cdot C_3N_3(CCl_3)_2$. The substances mentioned in this paragraph are, as a rule, easily decomposed by alkalis; bromoform and ammonium bromide are usually produced, and, if alcohol is present, a carbamine.

When phenylhydrazine is introduced beneath an ethereal solution of polymeric tribromacetoneitrile, a substance, $C_{10}H_8N_6Br_3$, is formed, which crystallises in white needles and melts at 210° . It is possibly

a triazole-derivative, with the constitution $CBBr_3 \cdot \begin{array}{c} N=C-NPh \\ | \quad | \\ C \quad N \\ | \quad | \\ N-C-NH \end{array}$;

aqueous potash decomposes it into phenylhydrazine and cyanuric acid. Under some circumstances, no such derivative is obtained, but only *phenylhydrazine hydrobromide*, $N_2H_3Ph \cdot HBr$, melting at 204° . From polymeric trichloroacetoneitrile, no triazole derivative was obtained, but only phenylhydrazine hydrochloride, melting at 240° .

The action of nitrous acid on amidodiperbromomethylcyanidine results in a complete breaking down of the latter substance. The

same is usually the case with the corresponding chloro-derivative, but, if the reaction is carried out in chloroform solution, a substance, $C_2N_2Cl_2(OH)_2$, is obtained in slender, white needles, melting at 155° ; it is soluble in alkalis, and yields a diethylic ether melting at 212° .

C. F. B.

Synthesis of Unsaturated Alcohols. By G. WAGNER (*Ber.*, 27, 2434—2439).—Unsaturated alcohols were obtained by adding a mixture of an aldehyde and allylic iodide to zinc shavings. When oxidised with permanganate, they yield glycerols and β -hydroxy-acids, together with some fatty acids, $R \cdot CHO + CH_2I \cdot CH \cdot CH_2 \rightarrow R \cdot CH(OH) \cdot CH_2 \cdot CH \cdot CH_2 \rightarrow R \cdot CH(OH) \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH \rightarrow R \cdot CH(OH) \cdot CH_2 \cdot COOH + CO_2$.

Acetaldehyde yields *methylallylcarbinol*, a liquid boiling at 115 — 116° under 750 mm. pressure, and with sp. gr. 0.852 at $0^\circ/0^\circ$, 0.834 at $20^\circ/0^\circ$. Its *acetate* boils at 133° under 743 mm. pressure, and has sp. gr. 0.911 at $0^\circ/0^\circ$, 0.891 at $20^\circ/0^\circ$. Both these compounds yield oily *dibromides*. The oxidation of the alcohol has already been described (*Abstr.*, 1889, 231).

Valeraldehyde yields *isobutylallylcarbinol*, boiling at 162 — 163° under 748 mm. pressure, and with sp. gr. 0.854 at $0^\circ/0^\circ$, 0.834 at $21^\circ/0^\circ$; the *acetate* boils at 178.5 — 179.5° under 760 mm. pressure, and has sp. gr. 0.889 at $0^\circ/0^\circ$, 0.871 at $20.5^\circ/0^\circ$. When oxidised, the alcohol yields the *glycerol*, which melts at 50° , and *hydroxyisovaleric acid* (a liquid, the calcium salt of which crystallises with H_2O), together with isovaleric and formic acids.

Cenanthaldehyde yields *hexylallylcarbinol*, boiling at 211 — 212° under 751 mm. pressure, and having sp. gr. 0.850 at $0^\circ/0^\circ$; the *acetate* boils at 224 — 225° under 738.7 mm. pressure. When oxidised, the alcohol yields the *glycerol*, melting at 78° , β -*hydroxyisocaproic acid*, melting at 48 — 51° , and *cenanthylic acid*.

Oxymethylene yields, though less easily, *allylcarbinol* itself. This is a liquid which boils at 113.5° under 748 mm. pressure; its *dibromide* has sp. gr. 1.976 at $0^\circ/0^\circ$, and boils at 131 — 141° under 16 mm. pressure. The *acetate* boils at 125° under 750 mm. pressure, and has sp. gr. 0.934 at $0^\circ/0^\circ$; its *dibromide* boils at 143 — 144° under 23 mm. pressure, and has sp. gr. 1.762 at $0^\circ/0^\circ$. When oxidised, the alcohol yields the *glycerol* and formic acid; the former boils at 190 — 191° under 18 mm. pressure, and yields a *triacetate*, which boils at 163 — 164° under 17 mm. pressure, and has sp. gr. 1.155 at $0^\circ/0^\circ$. When oxidised under fitting circumstances, this *glycerol* appears to

yield a lactone, $O < \begin{array}{c} CH_2 \cdot CH \cdot OH \\ CO \cdot CH_2 \end{array}$, and in this respect differs from the other glycerols mentioned, which do not, like it, contain a second $-CH_2 \cdot OH$ group.

C. F. B.

Formation of Succinic acid and Glycerol in Alcoholic Fermentation. By J. EFFRONT (*Compt. rend.*, 119, 92—93).—Glycerol and succinic acid, although always amongst the products of alcoholic fermentation, are not always present in the same ratio. The proportion of these secondary products is small at the commencement

of fermentation, but increases towards the end. Determinations of the quantities of glycerol and succinic acid in worts fermented by yeast accustomed to fluorides gave the following results per 100 grams of sugar decomposed :—

	24 hrs.	48 hrs.	72 hrs.	96 hrs.
Glycerol.....	0.1503	0.3508	0.3992	0.81
Succinic acid....	0.02541	0.04755	0.06759	0.0924

The maximum quantities of glycerol and succinic acid are found when the power of the yeast is almost exhausted owing to the disappearance of the fermentable substances. It would seem, therefore, that the formation of these products is due to an enfeebled condition of the yeast, and yeasts accustomed to fluorides and with increased fermenting power (this vol., ii, 425) are towards the end of the process in much the same condition as ordinary yeast at the commencement of ordinary fermentation. C. H. B.

Levoglucozan. By TANRET (*Compt. rend.*, 119, 158—161).—When picein (this vol., i, 616) is heated in sealed tubes at 100° with 20 times its weight of barium hydroxide solution for four hours, it is converted into levoglucozan, which, after precipitation of the barium, removal of the piceol by means of ether, and concentration of the liquid to a syrup, is extracted by means of boiling ethylic acetate, and finally crystallised from water.

Coniferin and salicin also yield glucosans under similar conditions, but a much more concentrated barium hydroxide solution is required, from 30 to 40 hours' ebullition is necessary, and the products are difficult to purify.

Levoglucozan has the composition $C_6H_{10}O_5$, and cryometric determinations show that the molecular weight is 162. It forms, large, rhombic crystals (1.0164 : 1 : 0.5674), very soluble in water and alcohol, and slightly soluble in ether; sp. gr. = 1.59. When heated at 178°, it melts, and under low pressure at this temperature, it sublimes without decomposing. Its rotatory power is $[\alpha]_D = -66.5^\circ$ in a 10 per cent. aqueous solution, $[\alpha]_D = -81.5^\circ$ in a 50 per cent. aqueous solution, $[\alpha]_D = -70.5^\circ$ in an alcoholic solution, $[\alpha]_D = -77.5^\circ$ in a solution in ethylic acetate. The rotatory power shows no appreciable variation with either time or temperature.

Levoglucozan yields ordinary glucose when heated for some time with dilute acids. It does not reduce Fehling's solution, and is not fermented by beer yeast; it is not affected by emulsin, and is not precipitated by basic lead acetate nor ammoniacal lead acetate.

The *benzoyl*-derivative, $C_6H_4O_2(Obz)_3$, is obtained by the action of benzoic chloride in presence of sodium hydroxide solution, and is a white powder, which melts at 194°, and is only very slightly soluble in water, alcohol, or ether. The *acetyl*-derivative, $C_6H_4O_2(OAc)_3$, is obtained by the action of acetic anhydride in presence of a small quantity of zinc chloride, and crystallises in needles melting at 107—108°. In alcoholic solution, its rotatory power is $[\alpha]_D = -45.5^\circ$. It would seem from these results that glucosan behaves as a trihydric alcohol, but this conclusion is not yet definitely established.

C. H. B.

Synthetic Glucosides. By E. FISCHER and L. BEENSCH (*Ber.*, **27**, 2478—2486).—The synthetic glucosides described in this paper were prepared by the method already made known (this vol., i, 3).

Ethylglucoside, $C_8H_{11}EtO_6$, has now been obtained in the crystalline condition; the method is, however, somewhat lengthy and complicated. When pure, it crystallises in mammelated groups of colourless needles, and melts at 65° . An aqueous solution containing 9.47 per cent. was found to have a sp. gr. of 1.024, and a specific rotatory power at 20° $[\alpha]_D = +140.2^\circ$; birotation was not observed. It does not reduce Fehling's solution when boiled with it for a short time, and is hydrolysed with tolerable rapidity when warmed with acids, somewhat more slowly, however, by invertase at 50° . The behaviour towards yeast has already been described by Fischer and Thierfelder (this vol., i, 487).

Methylgalactoside, $C_6H_{11}MeO_6$, crystallises in delicate needles containing 1 mol. H_2O ; it has a sweet taste, is sparingly soluble in cold alcohol, and the anhydrous compound melts at 111 — 112° . An aqueous solution containing 9.92 per cent. has a sp. gr. of 1.0296, and a specific rotatory power $[\alpha]_D + 163.4^\circ$; birotation was not observed; it only reduces Fehling's solution when boiled therewith for a protracted period, is readily hydrolysed by dilute acids, but apparently not by invertase; it is not fermented by Froberg yeast.

Ethylgalactoside, $C_6H_{11}EtO_6$, forms colourless needles, melts at 138 — 139° (corr.), remains unaltered when treated with invertase or with Froberg yeast, and has a specific rotatory power $[\alpha]_D = +178.75^\circ$.

Benzylarabinoside, $CH_2Ph \cdot C_6H_5O_6$, crystallises in colourless needles, melts at 172 — 173° (corr.), has a faint bitter taste, is readily hydrolysed by acid but not by invertase, and is not fermented by Froberg yeast. An aqueous solution containing 1.03 per cent. had a specific rotatory power $[\alpha]_D = +215.2^\circ$.

Propylglucoside and *glycerylglucoside* (from glycerol and glucose) were only obtained in the amorphous condition.

Glucosidogluconic acid, $C_{12}H_{22}O_{13}$, is obtained by the interaction of glucose and gluconic acid, under the influence of hydrogen chloride, as an amorphous powder, consisting of a mixture of the acid and the lactone; it was isolated by a complicated process. An aqueous solution of this product was precipitated by basic lead acetate and basic lead nitrate. The salts are readily soluble in water and amorphous; the calcium salt was analysed. When the acid is warmed on the water bath with 5 per cent. sulphuric acid, it is hydrolysed, yielding glucose and gluconic acid. The calcium salt was found not to ferment with Froberg yeast, and to be unattacked by invertase. The authors consider that the acid is either a structural isomeride or a stereoisomeride of maltobionic acid; they have not succeeded in transforming the acid or its lactone into the corresponding sugar, which they conjectured might possibly turn out to be identical with isomaltose (Fischer, *Abstr.*, 1891, 412).

Galactosidogluconic acid, *arabinosidogluconic acid*, *glucosidoglycollic acid*, and *glucosidoglyceric acid* were also prepared.

A. R. L.

Some Osazones and Hydrazones of the Sugar Group. By E. FISCHER (*Ber.*, 27, 2486—2492).—When natural xylose is reduced by sodium amalgam, it yields a polyhydric alcohol, xylitol, which is optically inactive by intramolecular compensation; this substance was isolated in the form of a colourless syrup, containing only traces of ash constituents. If the latter is oxidised with bromine and soda, and the product (*i*-xylose) is treated with phenylhydrazine acetate in the usual manner, *i*-xylosazone, $C_{17}H_{20}N_4O_8$, is obtained: it crystallises in delicate, yellow needles, melts and decomposes at 210—215°, and its solution in glacial acetic acid is optically inactive.

According to Alechin (*Abstr.*, 1890, 733), melezitose decomposes on partial hydrolysis into glucose and turanose; an analysis of the amorphous sodium derivative of the latter by Alechin indicated that the sugar has the formula $C_{13}H_{22}O_{11}$. The author having been furnished with a specimen of turanose, prepared the osazone, which gave values on analysis agreeing with the formula $C_{13}H_{20}O_8(N_2HPh)_2$. It crystallises from hot water in nodular aggregates of very minute needles, which separate in a form resembling a jelly and are extremely like isomaltosazone; the pure compound melts and decomposes at 215—220°. Alechin's formula for turanose is therefore confirmed.

Arabinose parabromophenylhydrazine, $C_6H_{10}O_4 \cdot N_2H \cdot C_6H_4Br$ (compare *Abstr.*, 1892, 439), is obtained by mixing aqueous solutions of parabromophenylhydrazine acetate and arabinose; it melts at 165° (corr.) and dissolves in about 40 parts of water. The formation of this hydrazone may be used as a test for the presence of arabinose, the reagents used being a freshly prepared solution of parabromophenylhydrazine in 3·5 parts of 50 per cent. acetic acid and 12 parts of water, and a 1 per cent. solution of arabinose; these solutions are mixed in the proportions of 1 part of sugar to 2 parts of parabromophenylhydrazine. In this way, arabinose may be detected in presence of xylose. The parabromophenylhydrazine acetate solution must not be heated, on account of the ease with which the acetyl-derivative is formed.

Wohl (*Abstr.*, 1893, i, 294) found a value for the melting point of *i*-arabinosazone somewhat higher than that observed by the author (*ibid.*, 292), who, having now subjected this osazone to repeated recrystallisation from hot water, finds the melting point to be 169—170° (corr.).

A. R. L.

Action of Acids on Glycogen. By M. CREMER (*Zeit. Biol.*, 31, 181—182).—Glycogen was heated with oxalic acid; glucose and isomaltose (identified as their osazones) were found in the product, the isomaltose corresponding with 10 per cent. of the glycogen. Maltose was never obtained, and the opinion is expressed that in those cases in which maltose has been described as occurring after the action of acids or ferments on starch and glycogen, it has arisen secondarily from isomaltose.

W. D. H.

Action of Ferments and Cells on Sugars. By M. CREMER (*Zeit. Biol.*, 31, 183—190).—In view of recent discoveries relating to the carbohydrates, the paper discusses, with references to authors, the

possibility of ferments and living cells bringing about the conversion of one kind of sugar into another, and also the relationship of the carbohydrate groups. Special stress is laid on yeast-glycogen (a starch-like substance coloured brown by iodine), which is formed in the yeast cell after feeding on solutions of dextrose, cane sugar, or levulose. The hypothesis is advanced that the levulose is first changed into dextrose.

W. D. H.

Constitution of Iodide of Starch. By C. LONNES (*Zeit. anal. Chem.*, 35, 409—436).—See this vol., ii, 475.

Substitution of Alkyl Radicles in Union with Carbon and Nitrogen. By C. MATIGNON (*Compt. rend.*, 119, 78—79; and by BERTHELOT, *ibid.*, 79—80).—A question of priority. C. H. B.

Derivatives of Propylamine. By F. CHANCEL (*Compt. rend.*, 119, 233—235).—*Propylpropylidenamine*, $C_3H_7 \cdot N \cdot C_3H_7$, is readily obtained by the action of propaldehyde on propylamine. It is a colourless, mobile liquid with a very disagreeable ammoniacal odour; it boils at 102° under a pressure of 760 mm., and is only slightly soluble in water; sp. gr. at $0^\circ = 0.84$. The salts of this amine cannot be prepared because, in presence of acids, it regenerates propaldehyde and propylamine.

Propylacetamide, $CH_3 \cdot CO \cdot NHPr$, is obtained by the action of acetic chloride on propylamine in presence of dry ether, or more conveniently by the action of ethylic acetate on propylamine in sealed tubes at 140 — 150° . It is a colourless, somewhat syrupy liquid with a feeble odour, and boils without decomposing at 222 — 225° under ordinary pressure.

Dipropylacetamide, $CH_3 \cdot CO \cdot NPr_2$, is obtained by the action of acetic chloride on dipropylamine in presence of ether, but cannot be obtained from ethylic acetate even at 160° . It boils at 209 — 210° .

Tetrapropylcarbamide, $CO(NPr)_3$, is obtained by the action of carbonic chloride on dipropylamine in presence of benzene. The action is very energetic, and it is desirable to use a slight excess of dipropylamine, and to heat for a short time towards the end in order to prevent the formation of dipropylcarbamine chloride. Tetrapropylcarbamide is a somewhat syrupy liquid, with a burning taste, and an aromatic odour recalling that of menthol. It boils without decomposing at 258° under a pressure of 755 mm., and is insoluble in water, but soluble in alcohol and benzene; sp. gr. at $0^\circ = 0.905$.

C. H. B.

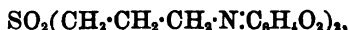
Sulphur Derivatives of Propylamine. By M. LEHMANN (*Ber.*, 27, 2172—2177).—*Diphthalimidopropylic bisulphide*,



which melts at 90 — 91° , is obtained by oxidising propylmercapto-phthalimide with iodine. When heated with hydrochloric acid at 180° , it yields the hydrochloride of diamidopropylic bisulphide; the *dibenzoyl*-derivative of this base forms colourless needles melting at 122° . When the latter substance is heated with phosphorus pentachloride, it yields mesophenylpentiazoline (*Abstr.*, 1893, i, 427). *Phthalyl*-

homotaurine, $C_6H_4O_2 \cdot N \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot SO_3H + 1\frac{1}{2}H_2O$, is formed when nitric acid is employed for the oxidation of propylmercaptophthalimide instead of iodine.

Diphthalimidopropyl sulphide, $S(CH_2 \cdot CH_2 \cdot CH_2 \cdot N \cdot C_6H_4O_2)_2$, melting at 118° , is obtained by the combined action of bromine and bromopropylphthalimide on propylmercaptophthalimide in alcoholic solution. The free base, *thiopropylamine* $(NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2)_2S$, is a colourless oil which boils at $247-248^\circ$ (753 mm.). On oxidising the sulphide with bromine, *diphthalimidopropylsulphoxide* is formed; it crystallises in needles which melt at $158-159^\circ$, and under the influence of hydrochloric acid yields the hydrochloride of *diamidopropylsulphoxide*; the picrate melts at 208° . If the sulphide is oxidised with chromic acid, *diphthalimidopropylsulphone*,



is obtained, separating from nitrobenzene in colourless plates which melt at 173° ; the action of alcoholic potash results in the formation of *propylsulphonediphthalamidic acid*,



The acid melts at $181-186^\circ$, and yields *diamidopropylsulphone hydrochloride*, with elimination of phthalic acid; this salt melts at $203-206^\circ$, and the *picrate* forms orange needles which melt at $192-197^\circ$.

Diphthalimidoethylpropyl sulphide is prepared by acting on propylmercaptophthalimide with bromethylphthalimide and bromine in alcoholic solution; it forms colourless needles which melt at $123-124^\circ$.

w-Amidopropylpiperidine, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C_5NH_{10}$, a colourless liquid boiling at 204° (751 mm.), is obtained by the interaction of bromopropylphthalimide and piperidine; the *picrate* forms golden-yellow prisms which melt at 209° .
M. O. F.

Octomethylenediamine. By M. VAN BREUKELEVEEN (*Rec. Trav. Chim.*, 13, 34-35).—*Octomethylenediamine*, $NH_2 \cdot [CH_2]_8 \cdot NH_2$, is readily obtained by the action of an alkaline solution of sodium hypobromite on sebacamide (Abstr., 1892, 1180), and is separated by extracting with ether, evaporating the ethereal solution, and subjecting the residue to fractional distillation. It melts at $50-52^\circ$, boils at $236-240^\circ$ (uncorr.), and attracts carbonic anhydride rapidly from the atmosphere. The *platinochloride* is crystalline, and, on heating, commences to blacken at 230° .
H. G. C.

Ethanehydrazoethane. By C. D. HARRIES (*Ber.*, 27, 2276-2282).—When diformylhydrazine, obtained by warming hydrazine hydrate with formic acid, is treated with alcoholic soda in aqueous solution, it yields a mono- and a disodium salt. The former crystallises in slender, interlacing needles, the latter in long needles. Both salts are alkaline to turmeric, reduce Fehling's solution, and with warm water yield free hydrazine and sodium formate. The *lead salt*, $C_2H_4O_2N_2 \cdot Pb$, is obtained by adding basic lead acetate to a solution of either of the sodium salts; it is an amorphous, white precipitate, reduces Fehling's solution when warmed with it, and is scarcely altered by prolonged boiling with water.

Diformylethanehydrazoethane, $\text{CHO}\cdot\text{NEt}\cdot\text{NEt}\cdot\text{CHO}$, is obtained by heating the lead salt dried at 105° with sand, magnesium oxide, and ethylic iodide in a sealed tube for 20 hours at 110° . It is a viscid oil, boils at $120\text{--}130^\circ$ under 20 mm. pressure, is volatile with steam, and reduces Fehling's solution slowly when boiled with it. Besides this compound, diformylethylhydrazine is also formed during the reaction, and the residue, after treatment with strong potassium hydroxide, yields ethanehydrazoethane and ethylhydrazine.

Ethanehydrazoethane, $\text{NHET}\cdot\text{NHET}$, is obtained by heating the preceding compound with fuming hydrochloric acid, and then treating the cold solution with hydrogen chloride; the filtrate, when mixed with alkali and distilled, yields pure ethanehydrazoethane. This boils at $84\text{--}86^\circ$ under 758 mm. pressure, is a colourless, limpid, highly refractive liquid, has an ethereal and ammoniacal odour, and reduces Fehling's solution and silver nitrate. It closely resembles ethylhydrazine. The *hydrochloride* crystallises in beautiful plates, and melts at 160° . When heated with strong hydrochloric acid at $150\text{--}160^\circ$, it yields ammonium chloride and ethylic chloride. When treated with red mercuric oxide in aqueous solution, a strong smell of mercurydiethyl is observed, and on adding solid potash, a small quantity of an oil is precipitated; this boils at $65\text{--}70^\circ$, does not reduce Fehling's solution, and quickly reduces silver and mercury solutions; on analysis, it gave numbers which did not agree very well with the formula $\text{NEt}\cdot\text{NEt}$. When treated with sodium nitrite in hydrochloric acid solution, it yields ethylic nitrite and a small quantity of liquid which boils at 150° , has the properties of a nitroso-compound, but does not reduce Fehling's solution. E. C. R.

Direct Formation of β -Alkylhydroxylamines. By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 13, 46—49).—The β -alkyl derivatives of hydroxylamine may be readily obtained by boiling an aqueous solution of hydroxylamine with an alkyl iodide and a little methylic alcohol, the hydriodide of the base separating out in crystals, which, after washing with alcoholic ether, are quite pure. The *hydriodides* of β -methylhydroxylamine, $\text{NHMe}\cdot\text{OH}$, and of β -ethylhydroxylamine, $\text{NHET}\cdot\text{OH}$, have been prepared in this manner; they are not altered at 200° , and do not reduce silver nitrate, but at once decolorise Fehling's solution in the cold. The free β -hydroxylamines have been recently obtained by Kjellin, and the author has therefore not made any further experiments in this direction.

For the preparation of the β -alkyl-derivatives, it is not necessary to prepare pure hydroxylamine; a suitable solution is obtained by adding the equivalent quantity of strong potash to a concentrated solution of hydroxylamine hydrochloride, mixing with an equal bulk of alcohol, and filtering from the precipitated potassium chloride.

H. G. C.

Mesoxalic acid and Bismuth Mesoxalate. By H. CAUSSE (*Compt. rend.*, 119, 228—231).—The oxidation of glycerol becomes less violent in presence of bismuth nitrate, or some other metallic salt capable of forming insoluble compounds with the products of oxidation.

100 c.c. of nitric acid of sp. gr. 1.39 is mixed with 250 c.c. of a saturated solution of potassium nitrate, and the mixture is saturated with basic bismuth nitrate, and afterwards heated at 50° for half an hour in presence of excess of this salt. The filtered liquid is mixed with one-third its weight of glycerol of 30° B., and the mixture is distributed in quantities of 75 c.c. in flasks of 150 c.c. capacity. The flasks are gently heated until evolution of gas begins, and are then removed from the flame. The oxidation at first proceeds slowly, but eventually becomes very violent. When the liquid cools, brilliant white crystals separate, and are collected and washed with cold distilled water. This product is *basic bismuth mesoxalate*, $C_2H_2O_6Bi$; it crystallises in microscopic, rhomboidal plates which become yellow at $50-60^{\circ}$, and carbonise if the heating is prolonged. The salt has the general properties of bismuth salts, and is decomposed by hot water. Acids and alkalis decompose it, especially on heating, and the mesoxalic acid is destroyed. Acetic anhydride in sealed tubes at 100° dissolves the salt without decomposing it, and it separates unchanged when the liquid cools.

If the bismuth mesoxalate is suspended in water containing some potassium hydrogen carbonate, and treated with hydrogen sulphide, it yields mesoxalic acid, which can be recognised by the formation of its barium and silver salts, its action on Fehling's solution, and the formation of its compound with phenylhydrazine.

Potassium hydrogen mesoxalate, $C_2H_2O_6K + 2H_2O$, forms very deliquescent crystals; it has a strongly acid taste, and dissolves in water, but is insoluble in alcohol and in ether. *Potassium antimony mesoxalate*, $C_2H_2(SbO)KO + H_2O$, is obtained by boiling the preceding salt with antimony oxide; it forms microscopic prisms grouped in rosettes.

C. H. B.

Bromomesaconic acid. By A. MICHAEL and G. TISSOT (*Ber.*, 27, 2130).—The authors have prepared bromomesaconic acid in the same manner as Lossen and Gerlach (this vol., i, 441), and have examined the properties of the acid and its salts. Their results confirm those of Lossen and Gerlach, except with regard to the amount of water of crystallisation of the calcium salt, which they find to be $2H_2O$ instead of $1H_2O$.

H. G. C.

Preparation of Glutaric acid. By E. KNOEVENAGEL (*Ber.*, 27, 2345—2346).—It has been observed that primary and secondary amines induce the condensation of aldehydes with ethylic acetoacetate and ethylic sodiomalonate. When the latter is brought in contact with formaldehyde and a small quantity of diethylamine or piperidine, tetrathylic methylenedimalonate is formed; from this, glutaric acid may be obtained by heating it for six hours with aqueous hydrochloric acid.

M. O. F.

Oxamidedioxime. By A. F. HOLLEMAN (*Rec. Trav. Chim.*, 13, 80—87).—Oxamidedioxime, on oxidation with potassium ferricyanide in alkaline solution, yields ammonia, carbonic anhydride, and

nitrogen. By the action of bromine water on oxamidedioxime, a sparingly soluble crystalline compound is obtained in small quantity; it dissolves in alkalis, and the solution does not contain oxalic acid. *Oxamidedioxime nitrate*, $C_2(NO_2)_2(NH_2)_2 \cdot 2HNO_3$, is prepared by the action of dilute nitric acid (1 : 4) on the oxime; it crystallises in rhombic plates, and explodes at 72° . The compound is only stable when pure; by the further action of nitric acid, it is converted into nitrogen and carbonic anhydride. Oxamide and nitrous oxide are formed by the interaction of nitrous acid and oxamidedioxime. *Dibenzoyloxamidedioxime*, $NH_2 \cdot C(NO_2) \cdot C(NH_2) \cdot NO_2$, crystallises from glacial acetic acid in long needles melting at 222° ; it is insoluble in alkalis and mineral acids, with the exception of concentrated sulphuric acid, which converts it into benzoic acid, and it is not affected by bromine at ordinary temperatures. *Oximamidoxalic acid*, $NH_2 \cdot C(NO_2) \cdot COOH$, is formed, together with oxalic acid, ammonium chloride, and hydroxylamine hydrochloride, by the action of hydrochloric acid on oxamidedioxime, it decomposes violently at 158° , gives the reactions of the amidoximes, and, by the further action of hydrochloric acid, is converted into oxalic acid. The *silver salt* is explosive. *Oxamidedioxime picrate*, $C_2H_4N_4O_2 \cdot C_6H_3N_3O_7$, is deposited from water in orange-yellow crystals melting at 127° . The *phosphate*, $C_2H_4N_4O_2 \cdot H_3PO_4$, crystallises with difficulty in stellate needles, and decomposes at $70-80^\circ$.

Succinamidedioxime picrate, $C_4H_4[C(NH_2) \cdot NOH]_2 \cdot 2C_6H_3N_3O_7$, crystallises in long, yellow needles melting at 197° . The *phosphate*, $C_4H_{10}N_4O_2 \cdot 2H_3PO_4$, is deposited in hygroscopic plates, decomposing at 133° . Attempts to prepare the silver salts of the two amide-dioximes were not very successful; the oxalate appears to exist, but is very unstable; succinamidedioxime reduces silver solutions.

J. B. T.

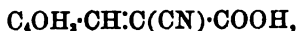
Amido-acids obtained by the Breaking Down of Vegetable Proteids. By E. FLEURENT (*Compt. rend.*, 119, 231—233).—When aspartic acid is heated with barium hydroxide solution under pressure, it is converted into oxalic, succinic, and acetic acids and ammonia; the conversion of the nitrogen into ammonia being complete only with an excess of barium hydroxide and under a somewhat high temperature, and after heating for many hours.

With glutamic acid, even after prolonged heating, only a small proportion of the nitrogen is converted into ammonia, and neither carbonic nor oxalic acid is formed.

It would seem that the differences observed between the decomposition of vegetable proteids and of animal proteids under the influence of barium hydroxide solution (this vol., i, 214) may be attributed to the intermediate formation of aspartic and glutamic acids, which afterwards decompose in a manner peculiar to themselves, the ratios being disturbed by the production of oxalic acid, and not carbonic acid as was previously supposed (*loc. cit.*). It would also seem that the constitution usually attributed to aspartic acid and analogous compounds requires reconsideration.

C. H. B.

Furalcyanacrylic acid and its Derivatives. By R. HEUCK (Ber., 27, 2624—2626).—*Furalcyanacrylic acid*,



is prepared by heating molecular proportions of furfuraldehyde and cyanacetic acid at 160° for half an hour; it crystallises from dilute alcohol in yellow needles, and melts at 218°. The *ethylic* salt is formed when a mixture of ethylic cyanate, furfuraldehyde, and acetic anhydride is heated at 180° for several hours (compare Carrick, Abstr., 1892, 1086; Fiquet, Abstr., 1893, i, 455). A more convenient method is to heat furfuraldehyde and ethylic cyanacetate for a few minutes with sodium dissolved in a small quantity of alcohol. Recrystallised from alcohol, it forms colourless needles melting at 94°, and boiling at 295—300°, undergoing partial decomposition. Addition of alcoholic potash to the cold solution develops a brilliant, blue coloration, rapidly changing to reddish-violet, and finally becoming brown. The *acetyl* derivative forms colourless needles which melt at 87°, resolidify at 90—95°, and again fuse at 160°.

The free acid loses carbonic anhydride at 220°, and an oil can be separated by distillation, having an odour suggestive of cinnamene, and consisting probably of furalcyanethylene. M. O. F.

Colour Reactions of certain Sulphur Compounds which occur with Aniline Bases. By A. HANTZSCH and H. FREESE (Ber., 27, 2529—2534).—The authors have failed to obtain the condensation products of paramidophenol and acetone or methyl ethyl ketone described by Haegerle (Abstr., 1892, 1451); the sole product was pure paramidophenol, which melted at 183°, was stable in air, and gave no coloration with calcium hypochlorite. Corresponding experiments with aniline gave a similar result. Specimens of commercial paramidophenol and aniline were found to contain 0.2 and 0.04 per cent. of sulphur respectively. Attempts to isolate the sulphur compound from aniline have not yet been successful, but, from its behaviour, there is little doubt that it is amidothiophen. The fractional crystallisation of aniline sulphate causes the thiophen-derivative to accumulate in the latter portions; it was converted into a *platinochloride*; the crystals of this are darker, and have a slightly different habit from those of aniline platinochloride, but the quantity obtained was very small. The more sparingly soluble aniline sulphate gave only a slight coloration with calcium hypochlorite. With aniline hydrochloride, the separation is less complete, and the thiophen-derivative accumulates in the first fractions.

Acetanilide, which melts at 115—116°, becomes brown, but is not hydrolysed by the action of concentrated sulphuric acid at 100°; the aniline obtained by hydrolysis of the residue with hydrochloric acid is almost pure.

An incomplete separation of aniline and amidothiophen is accomplished by fractional distillation, either alone or in a current of steam; the first fractions of the aniline are the purer.

The best method for the purification of aniline consists in boiling it for some time with acetone.

It is interesting to contrast these observations with those of V. Meyer, which led him to the discovery of thiophen in benzene.

J. B. T.

Aromatic Nitro-derivatives. Dinitrobenzenes. By C. A. LOBBY DE BRUYN (*Rec. Trav. Chim.*, 13, 101—147).—The separation of orthodinitrobenzene from the residue obtained during the manufacture of metadinitrobenzene has been previously described (*Abstr.*, 1893, i, 256). A detailed account of the preparation of paradinitrobenzene from quinonedioxime by Nietzki and Guitermann's method (*Ber.*, 21, 428) is given; the yield is 50—55 per cent. of the oxime. At 18°, the sp. gr. of metadinitrobenzene is 1·575, of orthodinitrobenzene, 1·59, and of paradinitrobenzene, 1·625; the sp. gr. increases therefore as the melting point rises. The boiling points of the three isomerides have been determined under various pressures, the ortho-derivative boils at 319° (773·5 mm.), the meta-compound at 302·8° (770·5 mm.); the para-compound at 299° (777 mm.), under 20—21 mm. pressure its boiling and melting points are identical, 172·1°. The solubility of the compounds in the following liquids has been determined—methylic, ethylic, and propylic alcohols, carbon bisulphide, benzene, ethylic acetate, toluene, carbon tetrachloride, and water; the results verify Carnelley and Thomson's rule that the solubility of isomeric compounds decreases as the melting points rise. Contrary to the statement in Beilstein's *Handbuch*, all three isomerides are volatile with steam, but under similar conditions about four times as much of the meta-compound volatilises as of the ortho-derivative, the para-compound is intermediate in this respect. Metadinitrobenzene is converted by the action of soda into metadinitroazoxybenzene, ammonia, nitrous acid, oxalic acid, and in small quantity, a brown, amorphous acid, which was not further investigated. Paradinitrobenzene, contrary to the statement of Hepp, is converted into paranitrophenol and nitrous acid by heating with soda (5—10 per cent.) during 3—6 hours; the yield is 75—80 per cent. of the theoretical. With more concentrated soda, the reaction is complex and the yield of nitrophenol smaller. *Paradinitroazoxybenzene* is formed in very small quantity along with the phenol; it crystallises in orange-red needles, and melts at 211°. By the action of ethylic alcoholic soda on metadinitrobenzene, dinitroazoxybenzene is readily formed; Michler and Klinger stated that this change was only accomplished in methylic alcoholic solution. Paradinitrobenzene resembles the ortho-compound in its behaviour towards alcoholic soda, one nitro-group being displaced by ethoxyl or methoxyl; the same change is produced by heating the dinitrobenzene with alcohol alone at 250°. *Paranitromethoxybenzene* and *paranitroethoxybenzene* melt at 52° and 58° respectively; both are crystalline. Metadinitrobenzene is not acted on by methylic alcoholic ammonia at 250°. Paradinitrobenzene is converted into a mixture of paranitroaniline and paranitromethoxybenzene or paranitroethoxybenzene by heating with methylic or ethylic alcoholic ammonia above 150°, but below this temperature no change occurs. From the author's experiments, it appears that the presence of ammonia lowers, by about 100°, the temperature at which the substitution of the group OMe for-

NO_2 takes place, and this temperature is only slightly below that at which the substitution of NH_2 for NO_2 occurs, a small increase in the temperature therefore causes the reverse change. Laubenheimer has shown that orthonitraniline is formed quantitatively from orthodinitrobenzene and alcoholic ammonia at 100° .

The action of chlorine and bromine on the three dinitrobenzenes has been previously described (Abstr., 1892, 305). With iodine, at a temperature of $300\text{--}330^\circ$, the dinitrobenzenes yield iodonitrobenzenes. The higher the atomic weight of the halogen, the less readily does it act on the dinitrobenzenes.

J. B. T.

Trinitrobenzene and 1:3:5-Dinitrophenol. By C. A. LOBBY DE BRUYN and F. H. VAN LEENT (*Rec. Trav. Chim.*, 13, 148—154).—The trinitrobenzenes, 1:3:5 (m. p. 122°) and 1:2:4 (m. p. $57\text{--}5^\circ$), accord with Carnelley and Thomson's rule. Their solubility in the following liquids has been determined: benzene, chloroform, methylic alcohol, ethylic alcohol, ether, and carbon bisulphide (compare preceding abstract). Tetranitroazoxybenzene and 1:3:5-dinitrophenol are formed by boiling 1:3:5-trinitrobenzene with sodium carbonate or soda. With alcoholic soda at ordinary temperatures, 1:3:5-dinitroethoxybenzene is obtained, and crystallises in yellow needles melting at 90° . Alcoholic ammonia gives a brownish-red coloration with symmetrical trinitrobenzene; on evaporation, a powder of the same colour is formed, but it could not be purified.

J. B. T.

Dinitrotoluenes. By C. HAEUSSERMANN and F. GRELL (*Ber.*, 27, 2209—2210).—The authors confirm Beilstein's statement (*Annalen*, 155, 25), that the product of the nitration of metanitrotoluene consists chiefly of dinitrotoluene [$\text{Me} : \text{NO}_2 : \text{NO}_2 = 1 : 3 : 4$], melting at 61° . A small quantity of 1:3:5-dinitrotoluene, which melts at 92° , is also formed, a mixture of these isomerides remaining liquid for a considerable period.

M. O. F.

Metanitrobenzylic Alcohol. By W. STAEDL (*Ber.*, 27, 2112).—This was prepared by P. Becker's method (*Ber.*, 15, 2090) from very pure metanitrobenzaldehyde. It solidifies in a freezing mixture, and is capable of forming very large crystals. It melts at 27° .

C. F. B.

Derivatives of Paracyanotoluene. By G. BANSE (*Ber.*, 27, 2161—2171).—*Nitrotoluenitrile* [$\text{CN} : \text{NO}_2 : \text{Me} = 1 : 3 : 4$], obtained by the action of fuming nitric acid on paratoluenitrile, forms yellowish-white needles, which melt at 107° . *ω -Chloronitrotoluenitrile* [$\text{CN} : \text{NO}_2 : \text{CH}_2\text{Cl} = 1 : 3 : 4$] is prepared in the same way from paracyanobenzylic chloride; it crystallises in colourless prisms, which melt at 84° . When reduced with tin and hydrochloric acid, this compound yields *amidotoluenitrile* [$\text{CN} : \text{NH}_2 : \text{Me} = 1 : 3 : 4$], melting at $81\text{--}82^\circ$. *ω -Chloronitrotoluic acid* [$\text{COOH} : \text{NO}_2 : \text{CH}_2\text{Cl} = 1 : 3 : 4$] is obtained from the nitrile by the action of fuming hydrochloric acid at 100° ; it melts at $140\text{--}141^\circ$, and forms a silver salt, which decomposes at 157° . The *amide* melts at 125° . The acid just

described reacts with aniline, forming *w*-anilidonitrotoluic acid [$\text{COOH} : \text{NO}_2 : \text{CH}_2\text{NPh} = 1 : 3 : 4$], a basic substance, which melts and decomposes at 160° ; the *hydrochloride* melts at 209° . With phenylhydrazine, the chloronitrotoluenitrile mentioned above forms *w*-phenylhydrazidonitrotoluenitrile, which melts at 207° , whilst with potassium phthalimide the corresponding *phthalimido*-derivative is formed, melting at 194° . From this substance, on hydrolysis, and elimination of the phthalyl group, *nitrobenzylaminocarboxylic acid* [$\text{COOH} : \text{NO}_2 : \text{CH}_2\text{NH}_2 = 1 : 3 : 4$], is obtained; it crystallises in nacreous plates, which melt at 243° ; the *hydrochloride* melts at 249 – 250 . *Cyanonitrobenzyllic acetate* [$\text{CN} : \text{NO}_2 : \text{CH}_2\text{OAc} = 1 : 3 : 4$], melting at 133° , is formed by heating an alcoholic solution of chloronitrotoluenitrile with sodium acetate; when hydrolysed, it yields *cyanonitrobenzyllic alcohol*, crystallising in yellowish-white needles, which melt at 139° . On reducing the acetate with tin and hydrochloric acid, *cyanamidobenzyllic alcohol* is formed; this melts at 102 – 103° .

Paracyanobenzyllic alcohol, which melts at 133 – 134° , is formed by the action of potassium carbonate on paracyanobenzyllic chloride; the *benzoate* melts at 123° . The *acetate* forms colourless leaves, which melt at 71 – 72° and yield parahydroxymethylbenzoic acid when hydrolysed; the nitration of the latter gives rise to a *dinitro*-derivative, which melts at 119 – 120° .

When paracyanobenzyllic alcohol is nitrated, *cyanonitrobenzyllic alcohol* [$\text{CN} : \text{NO}_2 : \text{CH}_2\text{OH} = 1 : 2 : 4$] is obtained, melting at 138° ; it differs from the isomeride just described in its behaviour under the influence of acids and alkalis, this treatment causing the displacement of the nitro-group by hydroxyl, with subsequent hydrolysis of the resulting nitrile. *Cyanohydroxybenzyllic alcohol*



the intermediate product in this reaction, melts at 169° .

Paracyanobenzyllic bromide is obtained by heating a mixture of paratoluenitrile and bromine in molecular proportion; it forms rhombic prisms, which melt at 115 – 116° . The *metanitro*-derivative melts at 106 – 107° .
M. O. F.

Synthesis of Symmetrical Carvacrol. By E. KNOEVENAGEL (*Ber.*, 27, 2347; compare *Abstr.*, 1893, i, 697).—Metacamphor (*Abstr.*, 1893, i, 419) when submitted to the action of bromine in acetic acid solution, yields an unstable dibromide; this readily loses the elements of hydrogen bromide, yielding symmetrical *carvacrol*, which melts at 54° and boils at 241° . It has the constitution [$\text{OH} : \text{Me} : \text{Pr}^s = 1 : 3 : 5$]; its odour is reminiscent of phenol, and it dissolves in alkalis with great readiness, but no coloration is developed with ferric chloride.
M. O. F.

Creosotes from Beech Tar and Oak Tar. By A. BÉHAL and E. CHOAY (*Compt. rend.*, 119, 166–169; compare this vol., i, 508).—Beech-tar creosote, boiling between 200° and 220° , contains in 100 parts, monophenols 39, guaiacol 19.72, creosol and its homologues

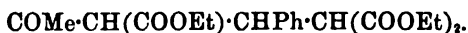
39·98. When fractionated, 367 parts, boiling at 210—220° (sp. gr. at 15° = 1·085), are obtained for every 1,000 parts boiling at 200—210°; sp. gr. at 17° = 1·085. The latter contains, in 100 parts, monophenols 39, guaiacol 26·48, creosol and its homologues 32·14.

Oak-tar creosote, boiling at 200—210°, sp. gr. 1·068, contains, in 100 parts, monophenols 55, guaiacol 14, creosol and its homologues 31.

The monophenols consist approximately of ordinary phenol 13, orthocresol 26, meta- and para-cresol 29, orthethylphenol 9, meta-xylene [1 : 3 : 4] 5, metaxylene [1 : 3 : 5] 2·5, other phenols 15·5 = 100·00.

Combining these figures with those previously given, it would seem that beech-tar creosote contains phenol 5·20, orthocresol 10·40, meta- and para-cresol 11·60, orthethylphenyl 3·06, metaxylene [1 : 3 : 4] 2·00, metaxylene [1 : 3 : 5] 1·00, various phenols 6·20, guaiacol 25·00, creosol and its homologues 35·00 = 100. These results are far from being in agreement with the accepted view that creosote consists chiefly of guaiacol. C. H. B.

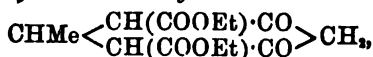
Derivatives of 1 : 3-Diketocyclohexane (Dihydroresorcinol). By E. KNOEVENAGEL (*Ber.*, 27, 2337—2345; compare Vorländer, this vol., i, 528).—The author studying the action of ethylic malonate on ethylic benzylideneacetoacetate in the presence of diethylamine, has arrived at substantially identical results with those described by Vorländer (*loc. cit.*), the product of the reaction being a crystalline compound which melts at 148°, and has the constitution



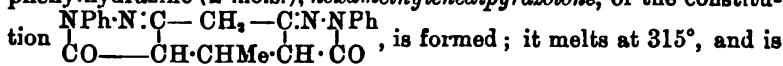
By the use of alcoholic potash in the place of diethylamine, *diethylic 5-phenyl-1 : 3-diketocyclohexane-4 : 6-dicarboxylate* is obtained in the form of its potassium salt; it melts at 156°. Hydrolysis of this substance leads to the formation of 5-phenyl-1 : 3-diketocyclohexane melting at 187—188° (compare Vorländer, *loc. cit.*; also Michael and Freer, *Abstr.*, 1891, 914). By the action of phosphorus pentachloride (2 mols.) on the latter compound, an oil is formed, probably having the constitution $\text{CHPh}\langle\begin{smallmatrix}\text{CH:CCl} \\ \text{CH:CCl}\end{smallmatrix}\rangle\text{CH}_2$; it is a highly refractive liquid boiling at 178—179° (22 mm.). Treatment with aniline gives rise to a substance which crystallises in lustrous scales, and decomposes without fusion. The product from ethylic benzylideneacetoacetate and ethylic malonate, under the influence of alcoholic hydrochloric acid, yields a compound which melts at 85°, and closely resembles β -phenyl- γ -acetylbutyric acid (Vorländer, *loc. cit.*); it differs from it, however, as regards solubility, and it will be the subject of future investigation.

In the above-mentioned reaction, ethylic ethylmalonate may be substituted for ethylic malonate; the compound formed melts at 154°. The product of the action of alcoholic hydrochloric acid on it melts at 90°. By acting on ethylic phenyldihydroresorcyate (Vorländer, *loc. cit.*) with phenylhydrazine, a substance of the formula $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2$ is obtained; it forms yellow scales, and melts at 130°.

Diethyl 5-methyl-1 : 3-diketocyclohexane-4 : 6-dicarboxylate,



is obtained by the interaction of ethylic malonate with ethylic ethylenediacetoacetate, in molecular proportion, in the presence of caustic potash; it melts at 85°, and, when crystallised from water, retains 1H₂O, this form melting at 75°. When this substance is heated with phenylhydrazine (2 mols.), *hexamethylenedipyrazolone*, of the constitution



is formed; it melts at 315°, and is insoluble in all indifferent solvents. Acids and alkalis dissolve it, however, the *sulphate* forming small, white needles; the *sodium* and *potassium* salts are hygroscopic. M. O. F.

New Synthesis of Phenol-alcohols. By L. LEDERER (*J. pr. Chem.*, [2], 50, 223—226).—Phenol-alcohols can be prepared, on the large scale also, by condensation of formaldehyde with phenols. The alcohol-group takes by preference the ortho- and para-positions, and it is possible, by varying the condensation agent, to obtain either an almost pure ortho-product, or a mixture of this with the para-isomeride. Below are given the melting points of various crystallised phenol-alcohols that have been obtained by this method; they give blue or green colours with ferric chloride, mixed sometimes with a shade of red.

Hydroxybenzylic alcohols. *Ortho (saligenin)*, 86°, sublimes readily. *Para.*, 110°. 1 : 2-*Hydroxymethylbenzylic alcohol*, 40°. 1 : 3-*Hydroxymethylbenzylic alcohol*, 107°. 1 : 4-*Hydroxymethylbenzylic alcohols*; (a) 107°, (b) 133°. 1 : 5 : 2-*Hydroxymethylpropylbenzylic alcohol*, 86°. 1 : 2 : 4-*Hydroxymethoxyallylbenzylic alcohol*, 37°. C. F. B.

Synthesis of Phenol-alcohols. By O. MANASSE (*Ber.*, 27, 2409—2413).—In this preliminary communication, the author states that he, like Lederer (preceding abstract), has obtained alcohols from phenols by condensing them with formaldehyde. The action takes place at the ordinary temperature when caustic soda is used as the condensing agent; potash, sodium carbonate, potassium carbonate, lime, zinc oxide, lead oxide, zinc dust, sodium acetate, or potassium cyanide may also be used.

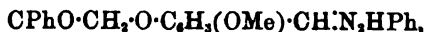
From phenol was obtained a mixture of para- (m. p. 111—112°) and ortho- (m. p. 82°) hydroxybenzylic alcohols. From guaiacol, vanillic alcohol (m. p. 115°), or an unstable compound (m. p. 110—111°) of this with formaldehyde (1 mol.). From paracresol, homosaligenin (m. p. 105°) [OH : Me : CH₂OH = 1 : 4 : 2]; from metacresol, a 1 : 4 : 3-isomeride (m. p. 117—118°), together with another of unknown constitution (m. p. 105°). From thymol, probably parathymotic alcohol (m. p. 120—121°) (Kobek, *Abstr.*, 1884, 56). From orthohydroxyquinoline, an alcohol, HO·C₆H₄·NH₂·CH₂·OH, which forms a compound (m. p. 141—142°) with 1 mol. of formaldehyde. β Naphthol yields no alcohol, but paradihydroxynaphthylmethane. C. F. B.

Eugenol and Isoeugenol. By A. EINHORN and C. FREY (*Ber.*, 27, 2455—2460).—Eugenol, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_3$, is converted into isoeugenol, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_3$, when it is heated quickly to 220° with 4 parts of caustic potash. When phosphorus oxychloride is added to a cooled solution of eugenol or isoeugenol, in aqueous soda, the *phosphates*, $\text{PO}[\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{C}_2\text{H}_5]_3$, are formed; in both cases they were obtained as oils. When 2:4:1-dinitrochlorobenzene and eugenol are dissolved in absolute alcohol, and potash is added to the solution, a yellow *dinitrophenylic eugenol ether*, $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{C}_2\text{H}_5$, melting at $114\text{--}115^\circ$, is formed; the yellow isomeride obtained from isoeugenol melts at $129\text{--}130^\circ$, and when oxidised, yields white *vanillin dinitrophenylic ether*, $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO}$, which melts at 131° , and can also be prepared by the action of dinitrochlorobenzene on vanillin. Picrylchloride and eugenol, when treated with caustic potash in alcoholic solution, yield yellow *picryleugenol*, $\text{C}_6\text{H}_3(\text{NO}_2)_3\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{C}_2\text{H}_5$, melting at $92\text{--}93^\circ$; isoeugenol yields a yellow isomeride which melts at $145\text{--}146^\circ$, and, when oxidised with chromic acid in acetic acid solution, yield *picrylvanillin*, $\text{C}_6\text{H}_3(\text{NO}_2)_3\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO}$, together with yellow *picrylvanillic acid*. The former melts at $114\text{--}116^\circ$, and can also be prepared from picryl chloride and vanillin; the latter melts at $184\text{--}186^\circ$, and is decomposed by potash into picric and vanillic acids. Picrylvanillin is also readily decomposed; with phenylhydrazine, it yields picrylphenylhydrazine (the yellow *acetyl-derivative* of which melts at 236°), and with aniline picrylanilide and vanillin.

C. F. B.

Phenacyleugenols and Acetonyleugenols. By A. EINHORN and C. v. HOFE (*Ber.*, 27, 2461—2466).—Eugenol and isoeugenol condense with bromacetophenone, or chloracetone, when the two substances are mixed in alcoholic solution, and alcoholic potash is added; phenacyl-derivatives, $\text{CPhO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{C}_2\text{H}_5$, or acetonyleugenol-derivatives, $\text{CMeO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{C}_2\text{H}_5$, being formed. The isoeugenol-derivatives, when treated with potassium permanganate, are oxidised to the corresponding vanillin or vanillic acid derivatives, the $-\text{C}_6\text{H}_3(=\text{CH}\cdot\text{CH}\cdot\text{CH}_3)$ group being converted into $-\text{CHO}$ or $-\text{COOH}$ respectively.

Phenacyleugenol (eugenolacetophenone) melts at $47\cdot5^\circ$, and forms a yellowish *phenylhydrazone*, melting at 82° , and an *oxime* melting at $81\text{--}82^\circ$. *Phenacylisoegenol (isoeugenolacetophenone)* melts at 83° , and yields a yellow *phenylhydrazone* melting at $115\cdot5^\circ$, and an *oxime* melting at $141\text{--}142^\circ$; boiling with alcoholic hydrochloric acid converts it into *di-isoeugenolacetophenone*, $\text{C}_{20}\text{H}_{20}\text{O}_6$, melting at $119\text{--}120^\circ$. When oxidised, it yields yellow *phenacylvanillic (acetophenonevanillic)* acid melting at 169° , and *phenacylvanillin (acetophenonevanillin)*, which melts at 128° , and forms a *monophenylhydrazone*,



melting at 161° , but no diphenylhydrazone; the vanillin derivative and its phenylhydrazone can also be prepared by the action of bromacetophenone on vanillin and its phenylhydrazone respectively.

Acetonylengenol is an oil, and its *phenylhydrazone* melts at 93° . *Acetonylisoengenol* is also an oil; its *phenylhydrazone* melts at 145° .

C. F. B.

Conversion of Eugenol into Isoengenol. By F. TIEMANN (*Ber.*, 27, 2580—2581).—This molecular rearrangement is dependent on the temperature to which the liquid is exposed, and not on the nature of the solvent employed. The conditions most favourable to the conversion of eugenol into isoengenol have been already described by the author (*Abstr.*, 1892, 45).

M. O. F.

α -Phenylethylamine. By M. KANN and J. TAFEL (*Ber.*, 27, 2306—2309).— α -Phenylethylamine, $\text{NH}_2\cdot\text{CHMePh}$, has already been prepared by the authors by reducing the hydrazone of acetophenone. It is very easily obtained by reducing either the oxime or hydrazone of acetophenone with sodium in boiling alcohol. The *nitrite*, obtained by shaking the hydrochloride with silver nitrite, melts at 75° with evolution of gas. The *acetyl compound* boils at $292\text{--}293^{\circ}$ under 752 mm. pressure, and melts at 57° . The *benzoyl compound* crystallises in white needles, and melts at 120° .

Benzylidene- α -phenylethylamine, obtained by the action of benzaldehyde on phenylethylamine, is a colourless oil. It decomposes when distilled under ordinary pressure, boils at $273\text{--}275^{\circ}$ under 14 mm. pressure, does not solidify at -1.5° , and is decomposed into its constituents when boiled with dilute acids.

α -Phenylethylcarbamide, obtained by the action of potassium cyanate on phenylethylamine hydrochloride, melts at 137° , and decomposes about 210° .

Di- α -phenylethylloxamide, obtained by warming α -phenylethylamine with ethylic oxalate on the water bath, sinters at 180° , and melts at 185° .

E. C. R.

γ -Phenylpropylamine and its Conversion into Allylbenzene. By L. SENFER and J. TAFEL (*Ber.*, 27, 2309—2313).—*Benzoyl- γ -phenylpropylamine*, obtained by the Schotten-Baumann method, forms crystalline crusts, and melts at $57\text{--}58^{\circ}$. *γ -Phenylpropylcarbamide*, obtained from the base in the usual way, crystallises in lustrous leaflets, melts at 143° , and decomposes, when heated above 200° , with evolution of ammonia. *γ -Phenylpropylphenylthiocarbamide*, obtained from the base and phenylthiocarbimide, crystallises in colourless needles, and melts at 103° .

γ -Phenylpropylamine, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, combines energetically with carbon bisulphide to yield a white, crystalline mass which melts at 90° , and, on analysis, gave numbers corresponding with the formula of phenylpropylamine phenylpropyldithiocarbamic acid, $\text{C}_{19}\text{H}_{21}\text{N}_2\text{S}_2$.

Dimethyl- γ -phenylpropylamine, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$, is a colourless liquid, boils at 225° under 754 mm. pressure, has a faint odour, and reacts strongly alkaline in aqueous solutions. The *platinochloride* melts at 149° . The *picrate* crystallises in thin needles, and melts at 99° .

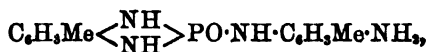
Trimethyl- γ -phenylpropylammonium iodide is obtained by boiling

phenylpropylamine with excess of methylic iodide and methylic alcohol in a reflux apparatus, and treating the product with excess of 10 per cent. sodium hydroxide. It melts at 175.5°.

Allylbenzene, $\text{CH} \cdot \text{Ph} \cdot \text{CHMe}$, is obtained by heating the preceding compound with excess of silver oxide, and, after distilling the product, treating it with dilute sulphuric acid and extracting with ether. It is a colourless liquid, boils at 174–176°, does not solidify at -16° , and has an odour resembling that of petroleum. The *dibromide* melts at 65–66°. When the sulphuric acid solution, obtained in the preparation of this compound is treated with solid potash, it yields dimethyl- γ -phenylpropylamine.

E. C. R.

Action of Phosphorus Tri- and Penta-chlorides on Ortho-toluylenediamine. By O. HINSBERG (*Ber.*, 27, 2178–2180).—A compound, which probably has the constitution



is obtained by the action of either of the phosphorus chlorides on ortho-toluylenediamine, the action in the case of phosphorus trichloride being accompanied by the liberation of hydrogen phosphide and amorphous phosphorus. It forms delicate, colourless needles, which melt at about 200°. Hydrolysis is effected by dilute acids or alkalis, phosphoric acid being eliminated with regeneration of the base. In the alcoholic solution, ferric chloride develops a green coloration, which becomes reddish-violet, finally changing to red when warmed.

M. O. F.

Stereoisomerism of the Diazo-compounds; Constitution of Isodiazo-compounds. By E. BAMBERGER (*Ber.*, 27, 2582–2595).—An attack is made on the system by which Hantzsch explains the existence of compounds isomeric with azo-derivatives (this vol., i, 452). The criticism is too detailed to be dealt with in an abstract, the author's main points, however, being the accord in which the nitrosamine formula stands with recorded facts, and the insufficiency of the evidence adduced by Hantzsch in support of his hypothesis.

M. O. F.

The "Stereoisomeric" Diazoamido-compounds of Hantzsch. By E. BAMBERGER (*Ber.*, 27, 2596–2601; compare Hantzsch, this vol., i, 549).—The existence of these substances is obviously of paramount importance to the controversy referred to in the preceding abstract. Careful examination of the so-called benzene-syndiazoanilide and paratoluenesyndiazotoluidide (*loc. cit.*), establishes their identity with bisdiazobenzeneanilide and bisparadiazotoluene-paratoluidide (Pechmann and Frobenius, this vol., i, 283) respectively. The two compounds are converted into diazoamidobenzene and diazoamidotoluene under the influence of alcoholic ammonia; this fact coincides with the observation of Hantzsch, the change having been regarded by this investigator, however, as a transformation of the syn- into the anti-modification.

M. O. F.

Constitution of Benzenediazoic Acid. By E. BAMBERGER (*Ber.*, 27, 2601—2611).—The evidence in support of the author's nitramine formula for this substance is recapitulated and followed by a criticism of the constitution advocated by Hantzsch (this vol., i, 456).
M. O. F.

Diazoamidobenzene. By W. BECKH and J. TAFEL (*Ber.*, 27, 2315—2316).—*Sodium diazoamidobenzene*, $\text{NNaPh}\cdot\text{N}\cdot\text{NPh}$, is obtained by dissolving sodium in an ethereal solution of diazoamidobenzene; on evaporation of the ether, it is deposited in long, reddish-yellow needles, which are unstable in moist air, being resolved into diazoamidobenzene and sodium hydroxide. Iodine removes sodium from the compound, whilst the action of benzoic chloride gives rise to *benzoyldiazoamidobenzene*, forming yellowish-brown needles, which melt and decompose at 131° . When boiled with alcohol, evolution of gas takes place, and the odour of aldehyde becomes perceptible; in this property it resembles acetyldiazoamidobenzene. If an ethereal solution of hydrogen chloride is added to benzoyldiazoamidobenzene dissolved in benzene, diazobenzene chloride is formed and may be separated by agitating with water, benzanilide remaining undissolved.
M. O. F.

Paradinitrodiazoamidobenzene: A Correction. By R. MELDOLA and F. W. STREATFIELD (*Ber.*, 27, 2201—2202).—The authors amend a statement of Pawlewski (*Ber.*, 27, 1565) to the effect that paraphenylenediamine is the sole product obtained by them on reducing the azo-compound in question. This is not the case, products resulting from reduction with sulphide of ammonium in alkaline solution having been already described by the authors (*Trans.*, 1886, 628). They attributed the magenta coloration observed on dissolving the azo-compound in alcoholic potash to the formation of an alkali salt, and do not regard it as indicating an initial stage of the reduction. In connection with this point, analogous salts have been described, and it is found that they are all coloured substances, the silver and cadmium salts especially exhibiting a brilliant red tint.
M. O. F.

Phenylhydrazine. By BERTHELOT (*Compt. rend.*, 119, 5—12).—Phenylhydrazine when exposed to air quickly becomes yellow; the change is more distinct if it is previously dissolved in water or dilute acids, brown insoluble matter separating from the solution. This change is due to oxidation, and is most marked when the solution of phenylhydrazine hydrochloride is mixed with sodium acetate; oxygen is absorbed and an equal volume of nitrogen is liberated, this ratio being maintained at every stage of the action, which is complete in 12 hours at 100° . Oily uncrystallisable diphenylhydrazine separates from the liquid.

Pure anhydrous phenylhydrazine when heated at 100° with oxygen in closed vessels absorbs 1.1 to 1.25 atoms of oxygen, and 1.6—1.7 atoms of nitrogen is liberated. The products are resinous, uncrystallisable, and insoluble in water.

Pure liquid phenylhydrazine absorbs moisture from the air, and after a few hours crystallises if the surrounding temperature is below 22° . The hydrate can also be obtained by mixing the compound with rather less than half its volume of water, and allowing the mixture to evaporate spontaneously; beautiful colourless crystals separate, which soon become yellow, and eventually orange, in consequence of slow oxidation. The most rapid method of preparing the hydrate is to mix 10 c.c. of phenylhydrazine with 0.9 c.c. of water. It has the composition $2C_6H_5N_2 + H_2O$, and melts at 24.1° , whilst anhydrous phenylhydrazine melts at 17.5° , and not at 23° as is commonly stated.

Calorimetric experiments give the following results.

Molecular heat of fusion of phenylhydrazine	—2.645 Cals.
Heat of formation of the hydrate from liquid constituents	+8.41 „
Heat of formation of the hydrate from liquid water and solid phenylhydrazine	+3.12 „
Heat of formation of the hydrate from solid constituents	+1.55 „
Heat of fusion of the hydrate	+8.04 „

The direct combination of liquid phenylhydrazine and water yields a liquid hydrate with development of heat = 0.37 Cal. If a fragment of crystallised hydrate is added, crystallisation commences immediately and proceeds slowly, even after the mass has apparently become solid. It is, therefore, practically impossible to determine the heat of formation of the solid hydrate by direct synthesis.

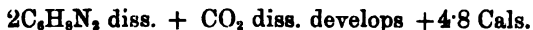
The heats of neutralisation are as follows.

	Liquid phenylhydrazine.		Dissolved phenylhydrazine.	
	1st equivt.	2nd equivt.	1st equivt.	2nd equivt.
Hydrochloric acid	+8.70 Cal.	—	+8.19 Cal.	—
Sulphuric acid	+9.11 „	+10.28 Cal.	+8.82 „	+9.99 Cal.
Acetic acid	+5.42 „	—	+5.13 „	—

In the case of the sulphate, the first equivalent of the base develops less heat than the second; in the case of the acetate, the addition of a second equivalent of acid causes a further development = 1.26 Cals., probably because the normal acetate dissociates in contact with water. An excess of phenylhydrazine causes a distinct increase in the heat developed on formation of the normal salts.

Phenylhydrazine does not react with carbonic oxide, and does not absorb carbonic anhydride from the air. Moreover the hydrochloride liberates only a small quantity of gas from solutions of normal sodium carbonate, and that very slowly; if, on the other hand, the hydrochloride is added to a solution of sodium hydrogen carbonate there is rapid evolution of gas, with development of heat = 3.1 Cal. for the complete reaction in presence of sufficient water to dissolve the whole

of the carbonic anhydride. For a complete reaction, as in the case of ammonium salts,



The difference between the heats of formation of the sulphate and chloride +1.21 Cal. is of the same order of magnitude as in the case of the stable alkali salts, but the difference between acetate and chloride is much greater, doubtless in consequence of the dissociation of the former, and the difference is still greater in the case of the carbonates. When a solution of phenylhydrazine sulphate or hydrochloride is mixed with sodium acetate, there is distinct absorption of heat, and with sodium carbonate this absorption is still greater.

These results afford further confirmation of the author's law, that in the case of mixtures of dissolved salts the strong acid unites with the strong base with almost complete formation of that salt which is most stable in presence of water and is also the salt with the highest heat of formation in the solid state. C. H. B.

Solubility of Phenylhydrazine in Aqueous Solutions of Salts of the Alkalis. By R. OTTO (*Ber.*, 27, 2131—2133).—The author finds that phenylhydrazine dissolves readily in aqueous solutions of salts of the sulphinic acids, sulphonic acids, higher fatty acids, gallic acids, and of salicylic acid. The phenylhydrazine is only extracted with difficulty from the solutions by means of ether. H. G. C.

Action of Phosphorus Pentachloride on Symmetrical Benzoylphenylhydrazine. By H. V. PECHMANN and L. SEEBERGER (*Ber.*, 27, 2121—2125).—The action of phosphorus pentachloride on symmetrical benzoylphenylhydrazine gives rise to a number of by-products in addition to the imidochloride already described (this vol., i, 240); these consist chiefly of benzoylhydrazides of phosphoric acid. The first product of the action is probably the *amidochloride*, $\text{CPhCl:N:NPh}\cdot\text{POCl}_2$, which has not, however, been isolated. It is a syrup, which is decomposed by water with re-formation of benzoylphenylhydrazine, but if left for a time, or on treatment with alcohol, it yields at least six different compounds.

When the ethereal solution is treated with methylic alcohol, or better with phenol, it is converted into the imidochloride, CPhCl:N:NPh , already described, which remains for the most part undissolved, whilst the solution contains the *lactone of symmetrical benzoylphenylhydrazidophosphoric acid*, $\text{CPh} \begin{smallmatrix} \text{N}\cdot\text{NPh} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{PO}\cdot\text{OH} \end{smallmatrix}$; this forms silky, matted needles or lustrous prisms, melts at 161° , and is resolved by boiling acids or alkalis into phosphoric acid and symmetrical benzoylphenylhydrazine. It dissolves in cold alkalis, but loses this property after treatment with potash and methylic iodide; the resulting neutral compound yields phenylhydrazine on hydrolysis, proving that the source of the acid hydrogen atom of the original compound is the phosphoric acid group.

Symmetrical disbenzoylphenylhydrazidophosphoric acid,
 $(\text{NH}\cdot\text{Bz}\cdot\text{NPh})_2\text{POOH},$

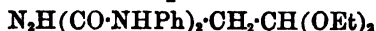
is obtained from the mother liquors of the foregoing compound, and may also be obtained in large quantity from the syrupy amidochloride by pouring it into an excess of methylic alcohol. It forms lustrous prisms or matted needles, melts at $131-132^\circ$, is soluble in alkalis, and reduces mercuric oxide in the cold. The *lactone* of this acid separates from the ethereal solution of the product of the action of phosphorus pentachloride and benzoylphenylhydrazine. If left for some days, it crystallises in small prisms melting at 164.5° . It is insoluble in alkalis, and does not reduce mercuric oxide. Another compound which appears to have the same composition is prepared by heating the benzoylphenylhydrazine with the pentachloride for several hours, and, after crystallising from a mixture of chloroform and alcohol, melts at 220° ; it also is insoluble in alkalis, and does not reduce mercuric oxide.

H. G. C.

Hydrazidoacetaldehyde II. By E. FISCHER and P. HUNSAIZ (*Ber.*, 27, 2203—2208; compare this vol., i, 169).—The authors prefer to express the constitution of acetalylphenylthiosemicarbazide by the formula $\text{NPh}\cdot\text{CS}\cdot\text{N}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, rather than by that already indicated (*loc. cit.*). They are led to this conclusion by the formation of acetalylphenylthiocarbamide under the influence of nitrous acid, and also by the fact that on elimination of two molecular proportions of alcohol, acetalylphenylthiosemicarbazide is converted into *phenyllithioamidodihydroimidazole*, $\text{CS} < \begin{smallmatrix} \text{N}(\text{NH}_2)\cdot\text{CH} \\ \text{NPh} - \text{CH} \end{smallmatrix}$, the reaction

being effected by heating in a closed tube with hydrochloric acid. The substance melts at 89° . It is indifferent towards Fehling's solution, and blackens mercuric oxide. The *hydrochloride* melts at 165° ; the *benzylidene*-compound forms shining yellow plates, which melt at $140-141^\circ$. Treatment with nitrous acid gives rise to phenylimidazole.

Acetalylphenylsemicarbazide, $\text{NPh}\cdot\text{CO}\cdot\text{N}_2\text{H}_3\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, is prepared by warming hydrazidoacetal with phenylcarbimide; it crystallises in colourless needles, which melt at $65-66^\circ$. If excess of phenylcarbimide is used, the *compound*



is formed, melting at $171-172^\circ$.

Acetylldimethylhydrazonium iodide, $\text{NH}_2\cdot\text{NMe}_2\text{I}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, is formed by the prolonged action of methylic iodide on hydrazidoacetal; it is converted into the *chloride* by agitation with silver chloride. The *platinochloride* separates from hot water in large, reddish-yellow plates which melt at 165° . A *substance* having reducing properties, and consisting most probably of the aldehyde $\text{COH}\cdot\text{CH}_2\cdot\text{NMe}_2\cdot\text{Cl}\cdot\text{NH}_2$, is formed from the chloride by the action of strong hydrochloric acid; its *platinochloride* is a bright yellow, amorphous powder.

M. O. F.

Phenylhydrazone of Salicylaldehyde. By H. BILTZ (*Ber.*, 27, 2288—2290).—An *isosalicylaldehyde phenylhydrazone* is obtained from

the mother liquors of the ordinary modification when salicylaldehyde, dissolved in light petroleum, is treated with an ethereal solution of phenylhydrazine. It melts at 104–105°, crystallises in triclinic needles, dissolves in sodium hydroxide, and is precipitated unchanged by acids; when warmed with alcohol it is converted into the ordinary modification melting at 142°.

A polymeric salicylaldehydephenylhydrazone, $(C_{13}H_{12}N_2O)_n$, is obtained when the hydrazone is heated with a 2 per cent. solution of potassium hydroxide in 50 per cent. alcohol. It crystallises from nitrobenzene in monoclinic crystals, and melts at 265°. E. C. R.

Benzhydroximic Chloride. By A. WERNER and H. BUSS (*Ber.*, 27, 2193–2201).—This compound was prepared with the object of converting it into phenylnitrolic acid by treatment with silver nitrite; the reaction, however, proceeds in a different direction, nitrous acid being eliminated with formation of benziledioxime peroxide.

Benzhydroximic chloride, $OH \cdot N : CPhCl$, is obtained by passing a current of dry chlorine gas into a well-cooled mixture of anti- or syn-benzaldoxime and chloroform, until the evolution of hydrogen chloride is accompanied by a change in the colour of the liquid from green to yellow. On allowing the chloroform to evaporate, benzhydroximic chloride is deposited in compact prisms which melt at 48°. Under other conditions, the action of chlorine on the synaldoxime leads to the formation of the antialdoxime hydrochloride, the final product consisting of benziledioxime peroxide.

Benzhydroximic chloride is stable towards water. Treatment with sodium carbonate removes hydrogen chloride, with formation of benziledioxime peroxide, whilst decomposition by sodium ethoxide gives rise to the formation of ethylbenzhydroximic acid and diphenylcarbamide. Towards bases, it displays great activity, ammonia producing benzenylamidoxime; the *dipropyl*-derivative of this, melting at 62–66°, is obtained by adding dipropylamine (2 mols.) to an ethereal solution of benzhydroximic chloride.

Dibenzhydroximic acid, $OH \cdot N : CPh \cdot OBz$, which melts at 95°, is prepared by the action of silver benzoate on benzhydroximic chloride; it, however, spontaneously undergoes molecular rearrangement, the isomeric dibenzhydroxamic acid, $OH \cdot CPh \cdot N \cdot O \cdot COPh$ (benzoyl benzhydroxamate), being formed.

It has already been mentioned that the peroxide of benziledioxime is obtained by the action of sodium carbonate on benzhydroximic chloride, hydrogen chloride being eliminated; an oily substance which rapidly solidifies, is first formed, and this is regarded by the authors as the intermediate product of the action, yielding benziledioxime peroxide by polymerisation. To this substance the authors assign the constitution $Ph \cdot C : NO$, a view which is strengthened by the formation of hydroxylamine on hydrolysis. The action of caustic potash on benzhydroximic chloride proceeds in two directions, either like that of sodium carbonate, or, with the displacement of chlorine by hydroxyl.

These observations lead the authors to conclude that the substance

obtained by the action of sodium carbonate on the oxime of hydroxy-isonitrosoacetone nitrite (Behrend and Schmitz, *Abstr.*, 1893, i, 304),

has the constitution
$$\begin{array}{c} \text{O} \cdot \text{N} : \text{C} \cdot \text{CMe} \cdot \text{N} \cdot \text{OH} \\ \text{O} \cdot \text{N} : \text{C} \cdot \text{CMe} \cdot \text{N} \cdot \text{OH} \end{array}$$

M. O. F.

Organometallic Compounds. By G. PÉRIER (*Compt. rend.*, 119, 90—92).—When acetanilide (2 mols.) and freshly-prepared anhydrous aluminium chloride (1 mol.) are gently heated together, a violent action takes place, with formation of a homogeneous liquid, which afterwards solidifies to a translucent, yellow mass, but there is no sensible evolution of hydrogen chloride. The same reaction takes place in presence of carbon bisulphide. The product, $(\text{C}_6\text{H}_5\text{ON})_2\text{Al}_2\text{Cl}_6$, is insoluble in all solvents which do not decompose it. With water, it yields aluminium chloride and acetanilide. Absolute alcohol dissolves it without any precipitation of aluminium hydroxide, but, on evaporation, acetanilide separates in crystals. Butyranilide forms a similar compound, $(\text{C}_{10}\text{H}_{13}\text{ON})_2\text{Al}_2\text{Cl}_6$.

Acetoparatoluidine and its substitution derivatives also yield analogous products, which decompose in contact with water or when exposed to air.

Anhydrous ferric chloride likewise combines with amides and amines, but the compounds, which probably have the composition $\text{R}_2\text{Fe}_2\text{Cl}_6$, are difficult to purify.

C. H. B.

Aromatic Chlorophosphines. By A. MICHAELIS (*Ber.*, 27, 2556—2559).—The author has previously suggested the term chlorophosphine for the group PCl_2 ; he now proposes that compounds in which this radicle is linked to oxygen shall be termed “*o*-chlorophosphines,” corresponding derivatives of phosphorus oxychloride being called “*o*-oxychlorophosphines,” and the acid derivatives of each “*o*-phosphinous acid” and “*o*-phosphinic acid” respectively. Thus $\text{OPh} \cdot \text{PCl}_2$ is phenol-*o*-chlorophosphine, $(\text{PhO})_3\text{P}$ is triphenol-*o*-phosphine, and $\text{PhO} \cdot \text{PO}(\text{OH})_2$ phenyl-*o*-phosphinic acid. Compounds containing chlorophosphine linked to nitrogen or sulphur are distinguished by the letters *n* or *s*, thus, $\text{NHPh} \cdot \text{POCl}_2$ is aniline-*n*-oxychlorophosphine, and $\text{NHPh} \cdot \text{PO}(\text{OH})_2$ aniline-*n*-phosphinic acid. The paper concludes with an abstract of Kunz's, Knauer's, and Schulze's investigations of these classes of compounds (following abstracts).

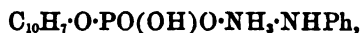
J. B. T.

NOTE.—This proposed use of *o*- is very misleading, as it is apt to be confounded with the *o*- used to signify ortho.—[EDITORS.]

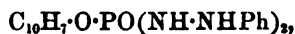
Phenol and Naphthol Chlorophosphines. By P. KUNZ (*Ber.*, 27, 2559—2565).—By the interaction of methoxybenzene or ethoxybenzene, phosphorus trichloride, and pure aluminium chloride, phenylchlorophosphine is formed, but, with commercial aluminium chloride, the methoxy- or ethoxy-phenylchlorophosphine, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{PCl}_2$, is obtained.

α-Naphtholchlorophosphine, $\text{C}_{10}\text{H}_7\text{O} \cdot \text{PCl}_2$, is prepared from phosphorus trichloride and *α*-naphthol, and from *α*-ethoxynaphthalene, phosphorus trichloride, and aluminium chloride; it is a colourless

liquid, soluble in anhydrous alcohol and ether, and boils at 174—176° (15 mm.), the sp. gr. = 1.0776. *α-Naphtholphosphinous acid*, $C_{10}H_7 \cdot O \cdot PO_2H_2$, prepared by the action of cold water on the preceding compound, is a colourless, crystalline powder, melting at 82°; like the chlorophosphine, it is resolved into phosphorous acid and *α-naphthol* by the prolonged action of water. The *phenylhydrazine salt*, $C_{10}H_7 \cdot O \cdot PO_2H \cdot NH_2 \cdot NHPh$, is a colourless powder, melting at 83°. *α-Naphtholoxychlorophosphine*, formed from *α-naphthol* and phosphorus oxychloride, is a thick, colourless liquid, boils at 325—327° or at 198—200° (20 mm.); the sp. gr. = 1.0889 at 15°. *Di-α-naphtholoxychlorophosphine* and normal *α-naphthol phosphate* are formed in small quantity with the preceding compound. *α-Naphtholphosphinic acid*, $C_{10}H_7 \cdot O \cdot PO(OH)_2$, prepared by the action of cold water on the chlorophosphine, is colourless and crystalline, melts at 142°, and is hydrolysed by warm water. The *phenylhydrazine salt*,



crystallises in thin plates, melting at 188°. The *diphenylhydrazine salt*, $C_{10}H_7 \cdot O \cdot PO(O \cdot NH_2 \cdot NHPh)_2$, is colourless, and melts at 147—148°. *Ethylic α-naphtholphosphinate*, $C_{10}H_7 \cdot O \cdot PO(OEt)_2$, is a colourless, viscid liquid, decomposing when distilled; its sp. gr. is 1.0441. *Ethylic di-α-naphtholphosphinate*, $(C_{10}H_7 \cdot O)_2PO(OEt)_2$, is obtained from alcohol and di-*α-naphtholoxychlorophosphine*; it crystallises in plates and melts at 31—32°. The *phenylhydrazone*,



prepared from the chlorophosphine and phenylhydrazine, is crystalline, and melts at 168—169°.

β-Naphtholchlorophosphine is a colourless liquid, formed in a similar manner to the *α*-derivative; it boils at 179—181° (15 mm.); its sp. gr. is 1.0781 at 15°. *β-Naphtholphosphinous acid* is colourless and crystalline, melts at 111°, and, like the chlorophosphine, readily becomes red. The *phenylhydrazine salt* melts at 98—99°. *β-Naphtholoxychlorophosphine*, from *β-naphthol* and phosphorus oxychloride, is colourless or slightly red, melts at 39°, and boils at 204—205° (20 mm.). *β-Naphtholphosphinic acid* is crystalline, and melts at 167°; it is hydrolysed by boiling with water, more rapidly by dilute acids, but is not attacked by alkalis. The *diphenylhydrazine* and the *hydrogen phenylhydrazine salts* are crystalline, and melt at 168° and 180° respectively. The *ethylyc salt* is a viscid liquid; its sp. gr. is 1.0439. The *phenylhydrazone* crystallises from glacial acetic acid and melts at 198°. *Di-β-naphtholphosphinic acid*, $PO(O \cdot C_{10}H_7)_2 \cdot OH$, is formed together with the oxychlorophosphine; it is crystalline, melts at 142°, and is not decomposed by boiling with water. The *phenylhydrazine salt*, $P(C_{10}H_7 \cdot O)_2 \cdot ONH_2 \cdot NHPh$, crystallises in long, thin plates, and melts at 183°.

J. B. T.

Chlorophosphines of Bibasic Phenols. By W. KNAUER (Ber., 27, 2565—2572).—*Resorcinoldichlorophosphine*, $C_6H_4(OPCl_2)_2$, is prepared by the prolonged action of phosphorus trichloride on

resorcinol; it is a colourless, highly refractive liquid, boiling at 240° (56 mm.); it fumes in air, is violently decomposed by water, even at low temperatures, and gives a white, unstable compound with chlorine. *Resorcinoldioxychlorophosphine*, $C_6H_4(OPOCl_2)_2$, from resorcinol and phosphorus oxychloride, is a fuming, colourless, viscid, highly refractive liquid, boiling at 263° (115 mm.) or at 216° (75 mm.); the sp. gr. = 1.643 at 15° ; it is resolved into resorcinol, hydrogen chloride, and phosphoric acid by the action of water. *Ethylic resorcinol diphosphinate*, $C_6H_4[OPO(OEt)_2]_2$, prepared by the action of alcohol on the preceding compound, is a viscid liquid, and decomposes on heating, or in presence of water.

Quinoldichlorophosphine resembles the resorcinol derivative in general properties, and is prepared in a similar manner; it is crystalline, melts at 65° , and boils at 200° (65 mm.). *Quinoldioxychlorophosphine*, from phosphorus oxychloride and quinol, forms hard, colourless crystals, melts at 123° , boils at 270° (70 mm.), and, by the action of alcohol, yields *ethylic quinoldiphosphinate*; it is a yellow liquid which decomposes when heated.

Secondary catecholchlorophosphine, $C_6H_4<\overset{O}{\underset{O}{\parallel}}\text{P}Cl$, prepared by heating catechol with phosphorus trichloride, forms colourless crystals, melts at 30° , boils at 140° (65 mm.), and is violently decomposed by water.

Tertiary catecholphosphine, $C_6H_4<\overset{O}{\underset{O}{\parallel}}\text{P}\cdot OC_6H_4\cdot O\text{P}<\overset{O}{\underset{O}{\parallel}}C_6H_4$, is formed together with the preceding compound, from which it is separated by fractional distillation; it is a yellow, viscid liquid, boils above 360° under reduced pressure, and is slowly decomposed by cold water; its sp. gr. is 1.353 at 15° . *Tertiary catecholphosphine*

oxide, $C_6H_4<\overset{O}{\underset{O}{\parallel}}\text{P}\cdot O\cdot C_6H_4\cdot O\text{P}<\overset{O}{\underset{O}{\parallel}}C_6H_4$, is obtained from phosphorus oxychloride and catechol as a viscid liquid, boiling above 360° under diminished pressure; it is hydrolysed by boiling water.

Secondary catecholoxychlorophosphine, $C_6H_4<\overset{O}{\underset{O}{\parallel}}\text{PO}Cl$, is prepared by the action of phosphorus oxychloride on the preceding compound; it crystallises in colourless needles, melts at 35° , boils at 162° (55 mm.), and is violently decomposed by water. J. B. T.

Aromatic Oxychlorophosphines. By A. MICHAELIS and G. SCHULZE (*Ber.*, 27, 2572—2579; compare this vol., i, 128).—*Diethylic anilidophosphate*, $NHPh\cdot PO(OEt)_2$, is obtained from aniline oxychlorophosphine by the action of ethylic alcohol. It forms large, white plates, which become reddish-yellow in the air and melt at 93° . The corresponding phenylic salt (Wallach and Heymer, *Ber.*, 8, 1235) is obtained by employing phenol; it melts at 129° . *Dicresylic anilidophosphate*, $NHPh\cdot PO(O\cdot C_6H_4Me)_2$, is formed when aniline oxychlorophosphine is heated with paracresol (2 mols.) at 220° . The crystalline form is hexagonal, and the substance melts at 133° .

When phosphorus oxychloride is heated with aniline (2 mols.)

for 48 hours in a reflux apparatus, dianilineoxychlorophosphine, $(\text{NHPh})_2\text{POCl}$, is formed. It melts at 174° , and is unattacked by water and alcohol. Alkalis dissolve it, the solution, when acidified, yielding dianilidophosphoric acid, $\text{PO}(\text{NHPh})_2\text{OH}$, in nacreous scales, which melt at 213° (compare Michaelis and v. Soden, Abstr., 1885, 1134). The copper salt forms bright blue, anhydrous plates. The phenylic salt melts at 125° .

Anilidophosphoric diparatoluidide, $\text{NHPh}\cdot\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$, is obtained by adding aniline oxychlorophosphine to fused paratoluidine (4 mols.); it forms silky needles, which melt at 168° . The trinitro-compound melts at 220° . Anilidophosphoric diorthotoluidide is obtained in a similar manner, and melts at 201° .

Paratoluidineoxychlorophosphine (this vol., i, 128), when treated with ethylic alcohol, gives rise to diethylic paratoluidophosphate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{PO}(\text{OEt})_2$, which forms colourless, feathery needles and melts at 98° ; the diphenylic and dicresylic salts melt at 134° and 161° respectively.

Dianilidophosphoric paratoluidide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{PO}(\text{NHPh})_2$, obtained by the mutual action of paratoluidine, oxychlorophosphine, and aniline (4 mols.), forms short prisms and melts at 168° . Diparatoluidineoxychlorophosphine, $\text{POCl}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$, is deposited from alcohol in small needles, and melts at 210° ; when dilute acids are added to its solution, diparatoluidophosphoric acid is formed (compare Rudert, Abstr., 1893, i, 324).

Orthotoluidineoxychlorophosphine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{POCl}_2$, melts at 91° ; it is readily decomposed by hot water. Alcohol converts it into diethylic orthotoluidophosphate, which melts at 95° . The analogous diphenylic and dicresylic salts melt at 176° and 161° respectively.

Diorthotoluidineoxychlorophosphine, $\text{POCl}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$, melts at 190° . The alkaline solution, when acidified, yields diorthotoluidophosphoric acid, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2\text{OH}$, which melts at 120° ; the copper salt crystallises from hot water in bluish-green needles.

Dianilidophosphoric orthotoluidide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{PO}(\text{NHPh})_2$, melts at 175° , and crystallises in short, thick prisms. M. O. F.

Paradiacetylbenzene. By H. INGLE (Ber., 27, 2526—2529; compare A. v. Baeyer, Abstr., 1892, 833).—Ethylic terephthalaldimalonate, $\text{C}_6\text{H}_4[\text{CO}\cdot\text{CH}(\text{COOEt})_2]_2$, prepared from terephthalic chloride and ethylic disodiummalonate, crystallises in long, silky needles melting at 110° . It is soluble in soda with a yellow coloration, and is slowly hydrolysed at ordinary temperatures; in alcoholic solution with ferric chloride a cherry coloration is produced. Paradiacetylbenzene (20—30 per cent.), acetylbenzoic acid (30 per cent.), and terephthalic acid (20 per cent.) are formed on heating ethylic terephthalaldimalonate with dilute sulphuric acid. Paradiacetylbenzene, $\text{C}_6\text{H}_4\text{Ac}_2$, crystallises in highly refractive, hexagonal prisms, melts at 114° , and gives no coloration with ferric chloride. The sodium hydrogen sulphite derivative is crystalline and melts at 182° . The phenylhydrazone crystallises in golden needles, the dioxime in colourless needles melting and decomposing at 240° . Acetylbenzoic

acid melts at 205° ; the *methylic salt* at 91° ; the *phenylhydrazine* crystallises in golden plates melting at 235° ; the *oxime* is deposited in plates, and melts at 254° .

Paradi- α -hydroxyethylbenzene, $C_6H_4(CHMe \cdot OH)_2$, is prepared by the reduction of *paradiacetylbenzene* with sodium amalgam; it is a viscid oil, readily soluble in water and alcohol, decomposes when heated under ordinary pressures, and is not attacked by potassium permanganate in the cold, but, on warming, is oxidised to terephthalic acid. Its taste is first sweet, then bitter.

Para- α -bromomethyl- α -hydroxyethylbenzene, $CHMeBr \cdot C_6H_4 \cdot CHMe \cdot OH$, is obtained by the action of concentrated hydrobromic acid on the preceding compound at ordinary temperatures, and crystallises in colourless needles melting at 136° . *Paradi- α -bromomethylbenzene*, $C_6H_4(CHMeBr)_2$, is prepared by the action of hydrogen bromide on *paradihydroxyethylbenzene* in glacial acetic acid solution; it is crystalline, and melts at 112° .

Paradivinylbenzene is formed by heating the preceding compound with quinoline under reduced pressure; it has an odour resembling that of petroleum, and boils at about 180° , but decomposes when heated under the ordinary pressure. The *tetrabromide*, $C_{10}H_{10}Br_4$, is crystalline, melts at 156.5° , and is converted into *paradi- α -bromomethylbenzene* by the action of hydrogen bromide in glacial acetic acid solution. Attempts to obtain a crystalline nitroso-chloride were unsuccessful.

J. B. T.

Existence of Meta- and Para-iodosobenzoic acid and of Metaiodoxybenzoic acid. By C. WILLGERODT (*Ber.*, 27, 2326—2337).—Contrary to the statement of Askenasy and Meyer (*Abstr.*, 1893, i, 508) and of Allen (*loc. cit.*, 578), meta- and para-iodosobenzoic acids are easily prepared.

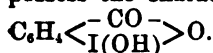
Metaiodosobenzoic acid, $IO \cdot C_6H_4 \cdot COOH$, is obtained by cautiously adding caustic soda to an aqueous solution of the iodochloride until the liquid is alkaline, when acid precipitates the iodosobenzoic acid from it; the latter is also formed by the prolonged action of water on the iodochloride. It is an amorphous, yellow substance, and explodes without detonation at 175 — 180° . If it is covered with water, the latter becomes acid towards litmus, but even after several days the acid retains its yellow colour. The powerful odour characteristic of iodoso-compounds is possessed in a high degree by this acid. It liberates iodine from potassium iodide, and when boiled for some hours with alcohol, the latter is oxidised to aldehyde, and *metaiodobenzoic acid* is formed. *Metaiodosobenzoic acid* is but slightly soluble in alcohol and ether, and insoluble in chloroform and benzene; in boiling glacial acetic acid it dissolves, and a yellow, amorphous substance is formed, which probably consists of the anhydride. A newly prepared specimen decomposed at 200° , but after some time effervescence took place at 190° . The original acid is soluble in strong sulphuric or in fuming nitric acid, and if boiled with dilute sulphuric acid, yields a partially crystalline mass which is inactive towards potassium iodide.

Metaiodoxybenzoic acid, $IO_2 \cdot C_6H_4 \cdot COOH$, is formed in association with *metaiodobenzoic acid* when the foregoing iodoso-compounds are heated in acid solution.

boiled for three hours with water; it is separated by means of its insolubility in boiling glacial acetic acid. It forms yellowish transparent prisms, and detonates at 243° . It dissolves with difficulty in boiling water, the solution depositing brilliant crystals on cooling; the aqueous solution develops in potassium iodide a yellow coloration which gradually deepens, being greatly intensified on the addition of glacial acetic acid. Metaiodoxybenzoic acid is insoluble in alcohol, ether, chloroform, and benzene, and is but slightly soluble in boiling acetic acid; it dissolves in cold caustic soda and in strong sulphuric acid.

Paraiodosobenzoic acid is prepared in a manner similar to that already described for the production of the meta-compound. It is a colourless, amorphous substance possessing the characteristic odour of iodoso-compounds. The point of explosion was found to be either 210° , 212° , or $203-205^{\circ}$, according to the method of preparation. It is insoluble in chloroform, benzene, and alcohol, but dissolves slightly in ether; the aqueous solution liberates iodine from potassium iodide, iodobenzoic acid being formed. Sulphuric and fuming nitric acids dissolve it readily without apparent change.

From a comparison of the properties of the three isomeric iodosobenzoic acids, the author considers that the meta- and para-compounds alone are true carboxylic acids, the ortho-derivative—which does not possess the characteristic odour—probably having the constitution



M. O. F.

Etherification of the Aromatic Hydroxyl Group. By J. HERZIG (*Ber.*, 27, 2119—2121).—In connection with the recent observation of Meyer and Sudborough (this vol., i, 463) on the abnormal behaviour of salicylic acid in etherification, the author points out that a similar abnormal behaviour is shown by a number of other substances in which the hydroxyl- and carboxyl-groups are in the ortho-position to one another. It appears, therefore, that in this position the two groups mutually influence one another in such a manner as to partially prevent etherification; the evidence at present available is not, however, sufficient to draw definite conclusions as to the exact nature of the interference which takes place.

H. G. C.

Hexahydroanthranilic and Hexahydrosalicylic acids. By A. EINHORN and A. MEYENBERG (*Ber.*, 27, 2466—2475).—When anthranilic acid is reduced with sodium in boiling amyl alcohol solution, small quantities of pimelic and hexahydrobenzoic acids are formed, but the main product is *hexahydroanthranilic acid*. This is neutral to litmus, and probably, therefore, has the structure of a betaine, $\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$; it melts and decomposes at 274° , and its *copper salt* crystallises with $2\text{H}_2\text{O}$. Its *ethyl salt* boils at $228-230^{\circ}$ (at $148-151^{\circ}$ under 30 mm. pressure), and forms a *hydrochloride*, which melts at 156° ; if the crude salt is distilled under atmospheric pressure, it is decomposed, probably by the moisture present, into ammonia and Δ^2 -tetrahydrobenzoic acid.

When hexahydroanthranilic acid is treated with nitrous acid, it is

converted into *hexahydrosalicylic acid*, identical with the acid obtained by Dieckmann (succeeding abstract) by reducing ethylic β -ketohexamethylenecarboxylate. This acid melts at 111° ; its *calcium salt* crystallises with H_2O ; its *barium salt* with $10\text{H}_2\text{O}$, of which 9 mols. are lost by efflorescence in the air, the tenth at $130\text{--}150^\circ$. Its *ethylic salt* boils at $120\text{--}121^\circ$ under 30 mm. pressure, and, when treated with Beckmann's reagent (*Annalen*, 250, 235), yields eventually ethylic β -ketohexamethylenecarboxylate. C. F. B.

Formation of Hexahydrosalicylic acid by Reduction of Ethylic β -Ketohexamethylenecarboxylate. By W. DIECKMANN (*Ber.*, 27, 2475—2477).—Hexahydrosalicylic acid is obtained by reducing ethylic β -ketohexamethylenecarboxylate (this vol., i, 173) with sodium amalgam. It is identical with the acid described by Einhorn and Meyenberg (last abstract). A. R. L.

Oxylactones derived from Phenylpyruvic acid. By C. ERLMEYER, jun., and N. KNIGHT (*Ber.*, 27, 2222—2226).—When phenylpyruvic acid is boiled with dilute sulphuric acid, a neutral substance of the formula $\text{C}_{17}\text{H}_{11}\text{O}_3$, is formed. In this reaction, a portion of the phenylpyruvic acid is decomposed with elimination of carbonic anhydride, whilst the remainder reacts with the phenylacetaldehyde thus produced to form the new compound, which is an oxylactone, $\text{CH}_2\text{Ph}\cdot\text{CH}\begin{smallmatrix} \text{CHPh}\cdot\text{CO} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$. The same compound is formed during the preparation of phenylpyruvic acid from α -benzoylamidocinnamic acid (Plöchl, *Ber.*, 16, 2878), and when ethylic phenylecyanopyruvate is heated with sulphuric acid. It forms a *sodium* compound, which dissolves readily in absolute alcohol, and is soluble in hot ether, but only very sparingly in water, forming a solution which is decomposed on boiling, phenylpyruvic acid and phenylacetaldehyde being formed. The sodium compound has a strongly alkaline reaction, and still contains the unbroken lactone ring. The *methyl*-derivative, $\text{C}_{18}\text{H}_{13}\text{O}_3$, prepared from the sodium compound, melts at 102° , whilst the *benzyl*-derivative crystallises in splendid prisms, and melts at 67° . Both these compounds contain the lactone ring. The lactone itself gives a green coloration with ferric chloride, whilst the methylic derivative does not.

Benzaldehyde condenses with phenylpyruvic acid in a similar manner, forming an oxylactone, $\text{CHPh}\begin{smallmatrix} \text{CHPh}\cdot\text{O} \\ \text{CO} \text{---} \text{CO} \end{smallmatrix}$, which crystallises in white needles, and melts at 206° . A. H.

Ethylic Phenacylcyanacetates. By T. KLOBB (*Compt. rend.*, 119, 161—162).—When ethylic sodiocyanacetate in alcoholic solution is mixed, in molecular proportion, with bromacetophenone, dissolved in three times its weight of dry ether, two products are formed, and may be separated by means of the difference in their solubilities in ether. *Ethylic diphenacylcyanacetate*, $\text{COOEt}\cdot\text{C}(\text{CN})(\text{CH}_2\cdot\text{COPh})_2$, crystallises from boiling alcohol in white needles, melts at 142° , and is only slightly soluble in most solvents. *Ethylic phenacylcyan-*

acetate, $\text{COOEt}\cdot\text{CH}(\text{CN})\cdot\text{CH}_2\cdot\text{COPh}$, is formed in smaller proportion, and is more difficult to purify. It crystallises from alcohol in white leaflets melting at 54° , and is also soluble in ether.

The lower homologues can be prepared from methylic cyanacetate in a similar manner. *Methylic diphenacylcyanacetate* forms microscopic needles, which melt at 195° , and are insoluble in ether, and only slightly soluble in boiling alcohol or benzene. *Methylic phenacylcyanacetate* crystallises from ether in nodules, and from alcohol in long needles; it melts at 54° , and is very soluble in the ordinary solvents.

The phenacylcyanacetates acquire a yellow colour in contact with an aqueous solution of potassium hydroxide, and the addition of an acid to the alkaline solution produces a blue precipitate. The diphenacylcyanacetates dissolve in alcoholic potash with formation of a deep blue solution, which yields a red precipitate when acidified.

C. H. B.

Ethylic Terephthalodicyanacetate. By J. LOCHER (*Compt. rend.*, 119, 162—165).—Terephthalic chloride can conveniently be prepared by heating together for several hours in a flask fitted with a reflux condenser terephthalic acid (1 mol.), phosphorus pentachloride ($3\frac{1}{2}$ mols.), and phosphorus oxychloride (3 mols.), allowing the liquid to remain for about 12 hours, and separating and fractionating the liquid portion.

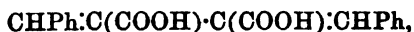
Dry and finely-powdered ethylic sodiocyanacetate (4 mols.) suspended in four times its weight of dry ether, is mixed with terephthalic chloride (1 mol.) dissolved in twice its weight of ether, and the mixture is gently heated. After 24 hours, the mixture is filtered, and the insoluble product washed with warm ether, dissolved in water, and mixed with acetic acid, which precipitates *ethylic terephthalocyanacetate*. The latter, purified by crystallisation from alcohol, forms long, white needles, which melt at 179° . It is insoluble in water, but dissolves in most organic solvents, and also in solutions of alkali carbonates or hydroxides, and in ammonia. It decomposes when heated at 100° , or when boiled with water or solutions of alkalis. With ferric chloride, the sodium salt gives the red colour which, according to Haller, is characteristic of the group $\text{CN}\cdot\text{CO}\cdot\text{CH}\cdot\text{COOEt}$.

Ethylic terephthalocyanacetate is a true bibasic acid. Its copper salt is a green crystalline powder containing $2\text{H}_2\text{O}$; the lead salt is white and amorphous; the di-silver salt is white and amorphous, and blackens when exposed to light; the ammonium salt is white and amorphous.

When boiled with water, ethylic terephthalocyanacetate splits up into terephthalic acid and ethylic cyanacetate, and does not yield a derivative analogous to cyanacetophenone. Sodium carbonate or sodium hydroxide produces a similar result. When boiled for two hours with phenylhydrazine (2 mols.), in presence of chloroform, it yields a hydrazone, $\text{C}_6\text{H}_5[\text{C}(\text{N}, \text{HPh})\cdot\text{CH}(\text{CN})\cdot\text{COOEt}]$, which crystallises from absolute alcohol in colourless crystals, melting at $260\text{--}261^\circ$; it is insoluble in water, and only slightly soluble in other solvents.

C. H. B.

Action of Sodium Ethoxide on Benzaldehyde and Ethylic Succinate. By H. STOBBE and E. KLOEPPEL (*Ber.*, 27, 2405—2409).—Benzaldehyde reacts much in the same manner as acetone (this vol., i, 15), when it (2 mols.) is mixed with ethylic succinate (1 mol.) in ethereal solution and sodium ethoxide (2 mols.) is added to the cooled solution. An acid, probably



melting and decomposing at 201°, is obtained; and, in addition, a mixture of phenylitaconic acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{COOH}):\text{CHPh}$, with some isomeric phenylitaconic acid (Fittig, 1890, 894; *Abstr.*, 1893, i, 691). C. F. B.

Substituted Isoimides of Phthalic acid. By S. HOOGWERFF and W. A. VAN DORP (*Rec. Trav. Chim.*, 13, 93—100; compare *Abstr.*, 1893, i, 599).—*Phthalomethylisoimide*, $\text{C}_6\text{H}_4\langle\text{C}(\text{NMe})_{\text{CO}}\rangle\text{O}$, prepared by heating phthalomethylamic acid with acetic chloride, is deposited from a mixture of ether and light petroleum in stellate crystals, and melts at 76·5—78·5°. *Phthalomethylimide* melts at 132°. The isomeride is a base, but its salts readily decompose in presence of water, forming phthalomethylamic acid.

Phthalobenzylisoimide, $\text{C}_6\text{H}_4\langle\text{C}(\text{NC}_6\text{H}_5)_{\text{CO}}\rangle\text{O}$, prepared in a similar manner from phthalobenzylamic acid, forms colourless crystals, melts at 81—82·5°, and resembles the methyl derivative in general properties.

Non-substituted isoimides have not yet been isolated, but impure hydrochlorides have been prepared and also *camphorisoimide aurochloride*, $\text{C}_9\text{H}_{14}\langle\text{C}(\text{NH})_{\text{CO}}\rangle\text{O}\cdot\text{H}\cdot\text{AuCl}_4$. In addition to the arguments previously advanced in favour of the constitution of the isomerides given above (*loc. cit.*), another is afforded by a comparison of their properties with those of acetamide and diacetamide; the basic properties of the isoimides preclude the presence of the group $\text{CO}\cdot\text{NH}\cdot\text{CO}$. *Phthalomethylamic acid* and *phthalobenzylamic acid* are readily prepared by dissolving phthalic anhydride in aqueous solution of methylamine or benzylamine and acidifying with hydrochloric acid.

A second camphormethylisoimide and two camphorisoimide hydrochlorides which give two acids of the formula $\text{CN}\cdot\text{C}_9\text{H}_{14}\cdot\text{COOH}$, have also been prepared, and will be described later. Their formation indicates that the carboxyl-groups in camphoric acid are unsymmetrical. J. B. T.

Action of Thionyl Chloride on Organic Compounds. By F. LOTH and A. MICHAELIS (*Ber.*, 27, 2540—2548).—Thionyl chloride and anisole, in presence of aluminium chloride, combine to form *thiomethoxybenzene*, $\text{S}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, which crystallises from benzene in colourless plates, melts at 46°, and is also formed from anisole

and sulphur monochloride or dichloride, and from thionyl chloride and mercuric dimethoxybenzene. *Tetrabromothiomeoxybenzene*, $S(C_6H_4Br_2OMe)_2$, is prepared by the action of bromine in glacial acetic acid on thiomethoxybenzene, and crystallises in colourless needles melting at 132° . Parabromochloromethoxybenzene, $C_6H_3BrClOMe$, is produced by the interaction of thionyl chloride and parabromomethoxybenzene.

Thiomethoxybenzene and tetrabromomethoxybenzene, on oxidation with nitric acid (sp. gr. 1.3) yield *thionylmethoxybenzene*,



and *thionyltetrabromomethoxybenzene*, $SO(C_6H_2Br_4OMe)_2$, respectively; the former crystallises in transparent, pale yellow rhombohedra melting at 96° , the latter in pale, lustrous plates melting at 155° ; it could not be obtained by the direct action of bromine on thionylmethoxybenzene. *Methoxybenzenesulphone*, $SO_2(C_6H_4OMe)_2$, is formed by the oxidation of thiomethoxybenzene with potassium permanganate; it crystallises in lustrous, transparent needles, and melts at 120° . The *bromo-derivative*, $OMe \cdot C_6H_4 \cdot SO_2 \cdot C_6H_3Br \cdot OMe$, is deposited in pearly plates melting at 170° .

The following ethoxy-derivatives were prepared in a similar manner to the corresponding methoxy-compounds. *Thioethoxybenzene*, $S(C_6H_4OEt)_2$, is deposited from benzene in colourless, quadratic crystals melting at 55° . The yield is 40 per cent. of the phenetol employed. *Tetrabromothioethoxybenzene*, $S(C_6H_2Br_4OEt)_2$, crystallises in needles, and melts at 142° . *Thionylethoxybenzene* crystallises in transparent rhombohedra melting at 116° . *Ethoxybenzenesulphone* is deposited in thin, lustrous plates, and melts at 263° . The *bromo-derivative*, $OEt \cdot C_6H_4 \cdot SO_2 \cdot C_6H_3Br \cdot OEt$, crystallises in milky plates, and melts at 185° .

Thionyl chloride acts directly on α -methoxynaphthalene and α -ethoxynaphthalene, whilst the β -derivatives require the presence of aluminium chloride; in all cases thio-derivatives are formed. *Thio- α -methoxynaphthalene*, $S(C_{10}H_7OMe)_2$, crystallises from chloroform in well-developed rhombohedra melting at 135° . *Thio- α -ethoxynaphthalene*, $S(C_{10}H_7OEt)_2$, forms lustrous, transparent crystals; it melts at 153° , and is sparingly soluble in chloroform. *Thio- β -methoxynaphthalene* crystallises in pearly, transparent plates. *Thio- β -ethoxynaphthalene* is deposited in lustrous crystals melting at 195° . By the action of nitric acid on the preceding naphthalene derivatives, crystalline compounds free from sulphur are formed. Chromic acid and alkaline potassium permanganate do not act on them, but on treatment with potassium permanganate in presence of glacial acetic acid two compounds are obtained, one crystallises in small, red needles and melts at 232° , whilst the other forms colourless needles, melts at 167° , and is probably either the sulphone of a thionaphthol ether, $SO_2(C_{10}H_7)_2O$, or a sulphur derivative of naphthaquinone. Dark, amorphous products are formed by the action of bromine on the thionaphthol ethers.

With thionylbenzene, thionyl chloride reacts like phosphoric chloride, forming chlororortho thiobenzene, $C_6H_4Cl \cdot SPh$, hydrogen

chloride, and sulphurous anhydride; with thionyl chloride in excess at higher temperatures, dichlorororthothiobenzene is obtained.

Bromochlorororthothiobenzene is prepared by the action of bromine on chlorororthothiobenzene dissolved in glacial acetic acid; it crystallises in lustrous, stellate plates, and melts at 110° . By the action of chlorine under similar conditions, di-, tri-, and tetra-chlorororthothiobenzenes are formed.

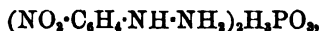
Benzaldehyde and thionyl chloride react to form benzal chloride. Sulphur monochloride does not act on benzaldehyde at ordinary temperatures; at 150° , benzoic chloride, sulphur, and hydrogen chloride are formed; in presence of aluminium chloride at ordinary temperatures, tarry substances are produced.

Thionyl chloride and acetone react violently, sulphurous anhydride and hydrogen chloride are evolved, and mesitylic oxide is formed, together with a disagreeably-smelling oil, which decomposes on distillation. Acetoxime and thionyl chloride react to form an unstable oily compound, which probably has the formula $\text{SO}(\text{NO}:\text{CMe}_2)_2$. No crystalline compounds could be obtained by the interaction of thionyl chloride and acetophenone.

J. B. T.

Thionyl Derivatives of Substituted Phenylhydrazines and of Hydrazinebenzoic acids. By J. KLEESEN (*Ber.*, 27, 2549—2556).—It has been shown by Michaelis and his pupils that aromatic hydrazines and ethylic metamidobenzoate react with thionyl chloride, the thionyl radicle displacing the hydrogen of the amido-group, but that metamidobenzoic acid does not form a thionylamine.

Metanitrothionylphenylhydrazone, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{SO}$, is prepared from metanitrophenylhydrazine hydrochloride and thionylaniline in presence of sodium acetate at ordinary temperatures, and crystallises in slender, pale yellow needles melting at 185° ; it is not altered by boiling water; with hot soda, a red coloration is produced, probably due to the formation of a *sodium salt*. At ordinary temperatures, it dissolves in soda with a yellow colour, which soon disappears, nitrophenylhydrazine being simultaneously deposited. By the action of bromine on the thionylhydrazone, metanitrodiazobenzene perbromide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Br}_3$, is formed. Thionyl chloride and the thionylhydrazone do not react at ordinary temperatures, but on warming metanitrodiazobenzene chloride is produced. Attempts to reduce the thionylhydrazone were unsuccessful. *Orthonitrothionylphenylhydrazone* resembles the meta-compound, and is prepared in a similar manner; it crystallises in small, red plates, melts at 128° , and does not yield diazo-derivatives by the action of bromine or thionyl chloride. *Orthonitrophenylhydrazine phosphite*,



crystallises in large, canary-coloured needles, and melts at 160° . *Parachlorothionylphenylhydrazone*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{N}:\text{SO}$, prepared in a similar manner to the nitro-compound, crystallises in slender, greenish-yellow needles, and melts at 159° . By the action of bromine, it yields parachlorodiazobenzene perbromide, and, by treatment with thionyl chloride, parachlorodiazobenzene chloride. *Parabromothionyl-*

phenylhydrazone, $C_6H_5Br \cdot NH \cdot N \cdot SO$, is prepared in a similar manner to the chloro-derivative, which it closely resembles in properties and reactions. It crystallises in small, yellow needles melting at 168° . *Dibromothionylphenylhydrazone*, $C_6H_5Br_2 \cdot NH \cdot N \cdot SO$, is prepared from thionylaniline and dibromophenylhydrazine, and crystallises in long, transparent, yellow, stellate needles melting at 99° . It readily sublimes, does not react with thionyl chloride or phosphorus chloride, and yields dibromodiazobenzene perbromide by the action of bromine. *Parabromorthonitrothionylphenylhydrazone*, $NO_2 \cdot C_6H_5Br \cdot NH \cdot N \cdot SO$, prepared in a similar manner to the preceding compound, forms small, pale yellow crystals, melts at 157° , and is converted into the corresponding diazo-derivative by the action of bromine and thionyl chloride.

Metathionylhydrazinebenzoic acid, $COOH \cdot C_6H_4 \cdot NH \cdot N \cdot SO$, formed from metahydrazinebenzoic acid and thionylaniline, crystallises in small, yellow plates, melts at 231° , and explodes when heated in a test-tube. It dissolves and decomposes in alkalis and alkali carbonates, and yields the diazoperbromide and diazochloride by the action of bromine and thionyl chloride respectively. *Parathionylhydrazinebenzoic acid* forms small, yellow crystals melting at 258° . *Orthothionylhydrazinebenzoic acid* crystallises in long, pale yellow needles, melts at 152° , and explodes at 155° , forming sulphurous anhydride and orthohydrazinebenzoic anhydride. Both the ortho- and para-compounds resemble the meta-derivatives in their properties and mode of formation. Attempts to prepare salts of these acids were unsuccessful.

J. B. T.

The Two Isomeric Forms of Diazobenzene Potassium Sulphite. By A. CLAUS (*J. pr. Chem.*, [2], 50, 239—240).—These two compounds, supposed by Hantzsch (this vol., i, 455) to be stereoisomeric only, the author regards as structurally isomeric. The orange-red unstable substance is diazobenzene potassiumsulphonate, $K \cdot SO_3 \cdot O \cdot N_2Ph$; the yellow stable one, potassium diazobenzene-sulphonate, $N_2Ph \cdot SO_2 \cdot OK$.

C. F. B.

Stereoisomerism of the Benzenediazosulphonic Salts. By A. HANTZSCH (*Ber.*, 27, 2099—2102).—E. Fischer suggested privately to the author the view of the constitution of these salts that has since been published by Claus (preceding abstract). This view is now discussed and rejected, the original (this vol., i, 453, 455) stereoisomeric formulæ being preferred.

C. F. B.

Partial Diazotisation of Benzidine. By E. TÄUBER (*Ber.*, 27, 2627—2631).—4:4'-*Amidodiazodiphenyl chloride*,



is obtained by mixing together solutions of tetrazodiphenyl chloride and benzidine hydrochloride in molecular proportion, and allowing the mixture to remain at 10 — 20° for two or three days. On boiling the solution, 4:4'-*hydroxyamidodiphenyl* is formed; it melts at 273° , and the most suitable solvents for crystallisation are alcohol and aniline. The *acetyl*-derivative melts at 225° , and when the alcoholic solution

of this substance is heated with ethylic bromide and caustic potash, 4:4'-ethoxyacetamidodiphenyl, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, is produced. It forms colourless needles which melt at 210° and its physiological action is comparable with that of phenacetin.

M. O. F.

Symmetrical Diamidoacridone. By M. SCHÖPF (Ber., 27, 2316—2321).—*Diamidoacridone*, $\text{NH}_2\cdot\text{C}_6\text{H}_3<\overset{\text{NH}}{\text{CO}}>\text{C}_6\text{H}_3\cdot\text{NH}_2$, is prepared by reducing tetranitrobenzophenone with stannous chloride and hydrochloric acid; the *stannochloride* is first formed, separating in fine, reddish-brown needles, which on prolonged warming with water yield metastannic acid and diamidoacridone hydrochloride in almost quantitative amounts. The base forms colourless needles, the melting point of which is not reached at 350° . The alcoholic solution exhibits bluish-violet fluorescence; the solution in phenol is yellow with green fluorescence, which is also shown by dilute solutions of the base in mineral acids. The *dihydrochloride* readily loses hydrogen chloride with formation of the *monohydrochloride*, $\text{C}_{18}\text{H}_{11}\text{N}_2\text{O}\cdot\text{HCl} + 4\text{H}_2\text{O}$, which separates from the aqueous solution of the normal salt in yellowish needles, the dilute solution of which exhibits a bluish-green fluorescence. The *platinochloride* forms microscopic orange needles. Symmetrical *diamidoacridine*, $\text{NH}_2\cdot\text{C}_6\text{H}_3<\overset{\text{N}}{\text{CH}}>\text{C}_6\text{H}_3\cdot\text{NH}_2$, is obtained by reducing diamidoacridone in alcoholic solution with sodium; it forms yellow needles which melt at 281° .

M. O. F.

Stereoisomerides of Carbodiphenylimide and Carboditolylimides. By C. SCHALL (Ber., 27, 2260—2263; compare Abstr., 1892, 1452; this vol., i, 135). The author maintains his view that α - and β -carbodiphenylimide and α - and β -carboditolylimide are stereoisomerides, against the criticism of Miller and Plöchl (Ber., 26, 1283). The two derivatives have the same molecular weight in benzene solution, and, therefore, are not polymerides.

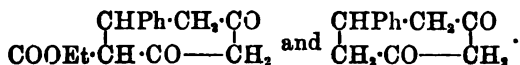
A. H.

Diphenols. By C. HÄUSSERMANN and H. TEICHMANN (Ber., 27, 2107—2109).—The diphenol melting at 123.5° , obtained with other products when phenol is fused with potash, is shown to be 3:3'-*dihydroxydiphenyl*, $\text{C}_{12}\text{H}_8(\text{OH})_2$. This substance was prepared both from orthodianisidine by removing the amido-groups and hydrolysing the resulting dimethylic ether, and from 3:3'-diamidodiphenyl by the diazo-reaction. It forms a *dimethyl*- and a *diacetyl-derivative* which melt at 36° and at 82.5° respectively.

C. F. B.

Action of Ethylic Sodiomalonate on Benzalacetone. By A. MICHAEL (Ber., 27, 2126—2130).—By the action of an ethereal solution of benzalacetone on ethylic sodiomalonate suspended in ether, a yellowish crystalline sodium salt is obtained, which on treatment with acids yields an ethylic salt having the composition $\text{C}_{10}\text{H}_{14}\text{O}_4$: this crystallises in small needles or prisms, melts at 144 — 145° , and yields a hydrazone crystallising in microscopic four-

sided colourless plates, which redden in the air. On treatment with hot potash, it undergoes hydrolysis and simultaneously loses carbonic anhydride, yielding the compound $C_{11}H_{12}O_2$, which forms quadric plates melting at $183-185^\circ$. These compounds are identical with those obtained by Michael and Freer (Abstr., 1891, 914) by the action of ethylic cinnamate on ethylic sodacetate, but the new synthesis is not in agreement with the constitutional formulæ previously assigned to them, which must, therefore, be abandoned. The most probable supposition is that they are derivatives of hexamethylene, the compounds $C_{10}H_{16}O_4$ and $C_{12}H_{18}O_2$, having the following constitutional formulæ:—



The latter compound is, on this assumption, a *phenyldihydroresorcinol*, and therefore corresponds with Merling's dihydroresorcinol, the diketone formula of which the author regards as more probable than Merling's (this vol., i, 177). H. G. C.

Derivatives of Diphenylmethane and of Benzophenone. By W. STAEDL (Ber., 27, 2109—2111).—2-Nitrodiphenylmethane when nitrated yields 2:4'-dinitrodiphenylmethane, melting at 118° , hitherto known as δ -dinitrodiphenylmethane. 4-Nitrodiphenylmethane yields 4:4'-dinitrodiphenylmethane (α) melting at 183° , together with some of the 2:4' (δ) isomeride. 3-Nitrodiphenylmethane yields 3:4'-dinitrodiphenylmethane, melting at $101-102^\circ$.

These diphenylmethane derivatives can be oxidised to the corresponding derivatives of benzophenone. Of the latter, 2-nitrobenzophenone, when nitrated, yields 2:2'-dinitrobenzophenone (γ) melting at 188° , and convertible into xanthone, together with less of the 2:3' (ϵ) isomeride, melting at 126° . 4-Nitrobenzophenone yields a mixture of 4:4' (α), 4:2' (δ), and 4:3'-dinitrobenzophenone, melting respectively at 189° , 196° , and 172° ; the last of these is a new substance. 3-Nitrobenzophenone yields 3:3'-dinitrobenzophenone (β) melting at $148-149^\circ$, together with small quantities of the 3:2' (ϵ) and 3:4' isomerides. C. F. B.

Condensation of Aromatic Alcohols with Nitro-hydrocarbons. By L. GATTERMANN and H. RÜDT (Ber., 27, 2293—2297).—2:4'-Dinitrodiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, is obtained when paranitrobenzylic alcohol or paranitrobenzylic acetate is heated with nitrobenzene and concentrated sulphuric acid in an oil bath for $1\frac{1}{2}$ hours at $130-140^\circ$. It crystallises in long, silky, colourless needles, and melts at $103-104^\circ$. When reduced, it is converted into 2:4'-diamidodiphenylmethane; this crystallises in lustrous leaflets, melts at $89-90^\circ$, and turns brown on exposure to air.

2:4'-Dinitrobenzophenone, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, is obtained by oxidising dinitrodiphenylmethane with chromic anhydride in acetic acid solution. It crystallises in stout, pale yellow needles, and melts at 175° . The 2:4'-diamidobenzophenone obtained from it by reduction, crys-

tallises in yellow prisms containing alcohol, which melt at 104° , and, after drying on the water bath, at $121-122^{\circ}$. The *diacetyl-derivative* crystallises in white needles and melts at 218° .

3 : 4'-*Dihydroxybenzophenone*, obtained from the amido-compound by means of the diazo-reaction, crystallises in colourless needles, and melts at 200° .

3 : 3'-*Dinitrodiphenylmethane*, obtained in a similar way to the 2 : 4'-compound, crystallises in small leaflets, and melts at 172° . The dinitrobenzophenone obtained from it melts at 151° ; the diamidobenzophenone crystallises in golden yellow needles and melts at $173-174^{\circ}$, and the dihydroxybenzophenone melts at $163-164^{\circ}$. These benzophenone derivatives are identical with those obtained by the nitration of benzophenone.

Dinitrophenyltolylmethane, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Me} \cdot \text{NO}_2$ [$\text{CH}_2 : \text{NO}_2 = 1 : 4$; $\text{CH}_2 : \text{Me} : \text{NO}_2 = 1 : 3 : 4$], obtained from paranitrobenzyllic acetate and orthonitrotoluene, crystallises in long, white needles, and melts at 143° .

Phenylnitrotolylmethane, $\text{CH}_2\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{Me} \cdot \text{NO}_2$, obtained from metanitrobenzyllic alcohol and orthonitrotoluene, crystallises in nacreous leaflets, and melts at $139-140^{\circ}$.
E. C. R.

Condensation with Formaldehyde. By M. SCHÖPFF (*Ber.*, 27, 2321—2326).—3 : 3'-*Dinitrodiphenylmethane* (m. p. 174°) is formed under certain conditions when formaldehyde is heated with nitrobenzene and sulphuric acid (D.R.P., 67,001). On reduction, it yields 3 : 3'-*diamidodiphenylmethane*, which melts at $47-48^{\circ}$.

Compounds resulting from the condensation of formaldehyde with ortho-, meta-, and paranitrophenols have already formed the subject of various patents (D.R.P., 72,490, 73,946, and 73,951), whilst from metanitrodiphenylmethane is obtained dinitrotetramethyldiamidodiphenylmethane [$\text{NMe}_2 : \text{NO}_2 : \text{CH}_2 = 1 : 3 : 4$]. Employing benzoic acid, *diphenylmethane-3 : 3'-dicarboxylic acid* is formed, soluble with difficulty in water, more easily in methylic and ethylic alcohols, the solutions exhibiting green fluorescence, which is also shown when acetone or glacial acetic acid is the solvent; it melts at $220-225^{\circ}$. For purposes of comparison, *diphenylmethane-4 : 4'-dicarboxylic acid* was prepared, and is found to melt at 290° . It is formed on hydrolysing 4 : 4'-*dicyanodiphenylmethane*, which may be obtained in large crystals melting at 165° . The solution in benzene is characterised by a green fluorescence.
M. O. F.

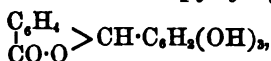
Condensation Products of Orthoaldehydic Acids with Phenols. By A. BISTRZYCKI and G. J. OEHLEBT (*Ber.*, 27, 2632—2640).—*Hydroxyphenylphthalide*, $\text{C}_6\text{H}_4 \text{---} \text{CO} \cdot \text{O} > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, is obtained by

the condensation of phthalaldehydic acid with phenol in the presence of strong sulphuric acid. It melts at $148-151^{\circ}$, and yields anthracene when distilled with zinc dust. The *nitro*-compound melts at $152-153^{\circ}$, and the *dibromo-derivative* at $223-224^{\circ}$. The *acetyl-derivative* melts at $125-126.5^{\circ}$.

Metacresylphthalide, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{CO}\cdot\text{O} \end{smallmatrix} > \text{CH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$, is prepared in the same way as the foregoing phthalide; it melts at 169—170°.

Resorcyphthalide, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{CO}\cdot\text{O} \end{smallmatrix} > \text{CH}\cdot\text{C}_6\text{H}_3(\text{OH})_2$, separates from dilute alcohol in fine, colourless needles, which lose 1 mol. H_2O at 120°, and melt at 130°. The *dibromo*-derivative melts at 197·5—199·5°.

Orcylphthalide, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{CO}\cdot\text{O} \end{smallmatrix} > \text{CH}\cdot\text{C}_6\text{H}_3\text{Me}(\text{OH})_2$, forms small, colourless plates, and melts at 241—242°, whilst *pyrogallylphthalide*,



melts at 175—177°.

The employment of opianic acid in place of phthalaldehydic acid gives rise to meconin-derivatives; nitro- and bromopianic acids, however, do not condense with phenol.

Hydroxyphenylmeconin, $\begin{smallmatrix} \text{C}_6\text{H}_3(\text{OMe})_2 \\ | \\ \text{CO} \text{ — } \text{O} \end{smallmatrix} > \text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, crystallises in nodular aggregates of needles, and melts at 160—170°; the *nitro*-compound melts at 177·5—179°, and the *dibromo*-derivative crystallises from glacial acetic acid in fine needles, melting at 195·5—196·5°.

Metacresylmeconin, $\begin{smallmatrix} \text{C}_6\text{H}_3(\text{OMe})_2 \\ | \\ \text{CO} \text{ — } \text{O} \end{smallmatrix} > \text{CH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$, is microcrystalline.

M. O. F.

Derivatives of Benzoylbenzoic Acid. By A. HALLER and A. GUYOT (*Compt. rend.*, 119, 139—142).—When phosphorus pentachloride is added to a carbon bisulphide solution of benzoylbenzoic acid, prepared by Friedel and Craft's method, there is an energetic action with evolution of hydrogen chloride and formation of a brown, oily liquid, which decomposes readily into benzoylbenzoic acid and hydrogen chloride. If this liquid is dissolved in benzene, and aluminium chloride is added to the solution, diphenylphthalide is obtained. It would follow that the product of the action of phosphorus pentachloride is $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CClPh} \\ \text{CO} \end{smallmatrix} > \text{O}$. Moreover, this view is supported by the fact that if in the preparation of diphenylphthalide from phthalic chloride, an insufficient quantity of aluminium chloride is added, benzoylbenzoic acid is also formed.

Dimethylamidodiphenylphthalide, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{COO} \end{smallmatrix} > \text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, is obtained by adding gradually to a solution of benzoylbenzoic acid in a large excess of dimethylaniline, the calculated quantity of phosphorus trichloride also dissolved in dimethylaniline, the temperature of the liquid not being allowed to rise above 50°. It crystallises from alcohol in white crystals, which melt at 119° and dissolve in most organic solvents, especially on heating. It combines with acids, and the hydrochloride forms white plates which lose their hydrochloric acid at 100° and dissociate readily in contact with water.

Dimethylamidotriphenylmethanecarboxylic acid,

is obtained quantitatively by the action of zinc on a hydrochloric acid solution of the phthalide, or better by the action of sodium amalgam on an alcoholic solution. It crystallises from xylene in small, white crystals, which melt at 190° and are only slightly soluble in ordinary solvents.

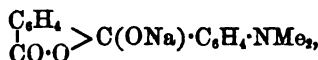
Dimethylamidophenylanthranol, $\text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2) \cdot \text{C}(\text{OH}) \text{---} > \text{C}_6\text{H}_4$, or

$\text{C}_6\text{H}_4 \cdot \text{C}(\text{Ph}(\text{C}_6\text{H}_4)) \cdot \text{C}(\text{OH}) \text{---} > \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, formed when the preceding compound is triturated with concentrated sulphuric acid, is a yellow powder which crystallises from boiling xylene in long, golden-yellow needles; it decomposes before it melts. C. H. B.

Amidobenzoylbenzoic acids and Dimethylanilinephthalein.

By A. HALLER and A. GUYOT (*Compt. rend.*, 119, 205—207).—If, in the preparation of benzoylbenzoic acid (preceding abstract) dimethylaniline is employed in place of benzene, the product is dimethylamidobenzoylbenzoic acid. The dimethylaniline must be dissolved in carbon bisulphide in order to avoid its decomposition by the aluminium chloride. The product is dissolved in dilute sulphuric acid, reprecipitated with ammonia, and purified by dissolution in sodium carbonate and crystallisation from alcohol.

Dimethylamidobenzoylbenzoic acid forms yellow, acicular or lozenge-shaped crystals which melt at 199° . It combines with acids and bases, forming two series of salts, which are generally readily crystallisable. The sodium salt, $\text{COONa} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, or



forms white crystals, soluble in water and alcohol, and when treated with sulphuric acid yields the original acid. The *methyl salt* is formed quantitatively when a solution of the acid in methylic alcohol is saturated with hydrogen chloride; it forms large, white crystals melting at 128° , soluble in all ordinary solvents, and regenerating the yellow acid when hydrolysed. The formation of this ethereal salt would seem to indicate that the dimethylamidobenzoylbenzoic acid has a carboxylic function.

The dimethylanilinephthalein obtained by Fischer by the action of phthalic anhydride or phthalic chloride on dimethylaniline in presence of zinc chloride, can easily be prepared by the action of phosphorus chloride on a mixture of dimethylaniline and dimethylamidobenzoylbenzoic acid, the yield being 90 per cent. of the calculated quantity.

Methylic tetramethyldiamidotriphenylmethanecarboxylate,

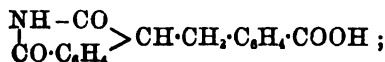
is obtained by the action of hydrogen chloride on a solution in methylic alcohol of the acid obtained by the reduction of dimethyl-

anilinephthalein with zinc and hydrochloric acid. It forms beautiful, white crystals, only slightly soluble in alcohol or ether, but much more soluble in chloroform, especially on heating. The salts usually crystallise well. The zincchloride crystallises from alcohol in white prisms.

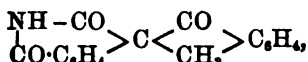
Diethylamidobenzoylbenzoic acid and its derivatives are obtained in a similar manner by substituting diethylaniline for dimethylaniline, and they have the same general properties. The acid forms yellowish crystals melting at 180°. *Diethylanilinephthalein* crystallises in needles.

C. H. B.

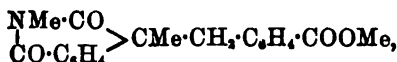
Ortho- α -tricyanodibenzyl. By S. GABRIEL and T. POSNER (*Ber.*, 27, 2492—2506).—The authors have improved the method of preparing ortho- α -tricyanodibenzyl (this vol., i, 279). When the tricyano-derivative is heated with hydrobromic acid of sp. gr. 1.47, the chief portion of the product consists of *dibenzylortho- α -tricarboxylimide* (*α -benzylhomophthalimidorthocarboxylic acid*),



this crystallises in white, microscopic, flat needles, melts at 242°, and dissolves in ammonia with an intense yellow coloration. If boiled with acetic anhydride, the *anhydro*-compound,

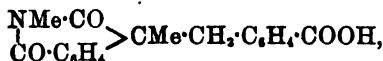


is formed; it melts at 263°. When *dibenzylortho- α -tricarboxylic imide* is heated with methylic alcohol, potash and methylic iodide, it yields *methylic α -methyl-dibenzylorthotricarboxylmethylimide*,



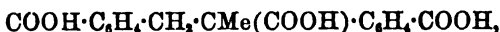
melting at 145°, together with *α -methyl-dibenzylortho- α -tricarboxylimide*, $\begin{array}{c} \text{NH}-\text{CO} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} > \text{CMe}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, melting at 233—236°. When

the former of these compounds is cohobated with hydriodic acid of 1.70 sp. gr., *α -methyl-dibenzylortho- α -tricarboxylmethylimide*,

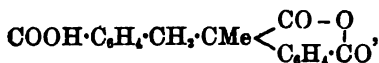


melting at 145—147°, is obtained. The synthesis of the last-named compound was attempted as follows:— *α -Methylorthohomophthalic acid* was evaporated to a syrup with an excess of aqueous methylamine, whereby *α -dimethylhomophthalimide*, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CHMe}\cdot\text{CO} \\ | \\ \text{CO}-\text{NMe} \end{array}$ (m. p. 64—66°), was obtained; this was converted by means of orthocyanobenzyl chloride into *orthocyanobenzyl- α -dimethylhomophthalimide*, $\begin{array}{c} \text{NMe}\cdot\text{CO} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} > \text{CMe}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$, melting at 117—118°, and the

latter, when heated with hydrochloric acid at 220°, gave rise to *α*-methyl dibenzylortho-*α*-tricarboxylic acid,



melting at 160°. The *anhydride* of the last-named acid,



melts at 183—184°, and is formed by heating the acid at 180°.

When the yellow ammoniacal solution of dibenzyltricarboxylimide is exposed to the air, a colourless ammonium salt, $\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_6$, separates, melting at 197—198°. The corresponding acid crystallises with 1 mol. H_2O , and appears to be *α*-oxydibenzylortho-*α*-tricarboxylaminelactonic acid, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CONH}_2) < \begin{array}{c} \text{CH}_2 \cdot \text{C}_6\text{H}_4 \\ \text{O} - \text{CO} \end{array}$, or

$\text{CONH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{COOH}) < \begin{array}{c} \text{CH}_2 \cdot \text{C}_6\text{H}_4 \\ \text{O} - \text{CO} \end{array}$; it melts and decomposes at 128—130°, and, if heated at 150—160°, it yields the lactone of *α*-hydroxydibenzyltricarboxylimide, $\begin{array}{c} \text{CO} - \text{O} \\ \text{C}_6\text{H}_4 \cdot \text{CH}_2 \end{array} > \text{C} < \begin{array}{c} \text{CO} - \text{NH} \\ \text{C}_6\text{H}_4 \cdot \text{CO} \end{array}$, melting at 239—241°.

When the lactonamic acid is boiled with alkali, ammonia is evolved, and the lactone of *α*-hydroxydibenzyltricarboxylic acid, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}(\text{COOH}) < \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} - \end{array} > \text{O}$, is formed; this melts and decomposes at 204—207°. In the hope of obtaining a salt of the corresponding acid, this lactone was boiled with barium hydroxide, and, after removing the excess of barium with carbonic anhydride, the filtrate was evaporated in a vacuum; the salt obtained had, however, the composition $\text{C}_{17}\text{H}_{10}\text{O}_6\text{Ba} + \text{H}_2\text{O}$, and was, therefore, a derivative of the lactone. If the lactone is heated at 220°, it yields J. Wislicenus' hydrodiphthalolactonic acid (*Ber.*, 17, 2181), which is also probably identical with the lactone (m. p. 201°) obtained by Ephraim (*Abstr.*, 1891, 1493; compare also Hasselbach, *Annalen*, 243, 253).

When the yellow solution of homophthalimide in potash is exposed to the air, the colour gradually disappears; no oxidation, however, takes place, homophthalamic acid being formed. If an alkaline solution of *α*-benzylhomophthalimide is exposed to the air it is oxidised, and *α*-hydroxydibenzylorthodicarboxylic acid,



is produced; this melts at 130—133°, and gives *α*-benzylphthalide (m. p. 60—61°) when heated at 180°. When a solution of *α*-benzylphthalide in potash is evaporated and the residue heated at 212°, the isomeric *stilbeneorthocarboxylic acid*, $\text{CHPh} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ (m. p. 158—160°), is formed.

A. R. L.

Action of Sodium on Monobromomesitylene. By P. JANASCH and M. WEILER (*Ber.*, 27, 2521—2526).—The authors have obtained two isomeric *dimesityls*, $\text{C}_{10}\text{H}_{12}$, by heating bromomesitylene

with sodium in presence of benzene or ether. The compound comprising the minor portion of the product is a solid, crystallising in small plates having a feeble fluorescence resembling that of anthracene; it melts at 78—79°, and boils at 330° (corr.). Two *tetranitro*-derivatives were prepared from this solid hydrocarbon, the one melting at 205—206° and the other at 158—160°; a *tetrabromo*-derivative melting at 170—171°, and a *hexabromo*-derivative melting at 280°, were also prepared. The major portion of the product consists of a liquid *dimesityl* which boils at 312—320°, and has a bluish fluorescence; it yields a *tetranitro*-derivative melting at 233°, and a complex mixture of bromo-derivatives which have not as yet been separated.

A. R. L.

***β*-Hydroxynaphthoic acid (m. p. 216°).** By H. GRADENWITZ (*Ber.*, 27, 2621—2624; compare R. Hirsch, *Abstr.*, 1893, i, 476; R. Möhlau, this vol., 138).—This acid is now known to be 2 : 3-hydroxynaphthoic acid (S. v. Kostanecki, this vol., i, 91). The author has reduced 2 : 3-chloronaphthoic acid with sodium amalgam, and obtained the dihydro-*β*-naphthoic acid which melts at 160°. The following derivatives of 2 : 3-hydroxynaphthoic acid are described for the first time.

1 : 2 : 3-*Bromhydroxynaphthoic acid*, $\text{OH} \cdot \text{C}_{10}\text{H}_7\text{Br} \cdot \text{COOH}$, is formed on brominating the acid in glacial acetic acid. It is deposited from acetic acid in long, yellow needles, and melts and decomposes at 233—235°; the *silver*, *lead*, and *barium* salts are not readily soluble.

The *monochlorinated acid* is obtained by the direct action of chlorine; it melts and decomposes at 231—233°. The *mononitro-acid* has been already described by S. Robertson (this vol., i, 137); its *methylic salt*, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6(\text{OH}) \cdot \text{COOMe}$, is obtained by nitrating the methylic salt of *β*-hydroxynaphthoic acid. It separates from acetic anhydride in lustrous yellow plates, and melts at 189°. When reduced with tin and hydrochloric acid, it yields the *methylic salt* of amido-2 : 3-hydroxynaphthoic acid; this crystallises from methylic alcohol in yellow needles melting at 106°. From this substance by oxidation, *methylic β-naphthaquinonecarboxylate*, $\text{C}_{10}\text{H}_6\text{O}_2 \cdot \text{COOMe}$, is obtained.

Methylic β-naphthaquinolcarboxylate [$\text{OH} : \text{OH} : \text{COOMe} = 1 : 2 : 3$] is formed when the methylic salt of amidohydroxynaphthoic acid is heated with dilute sulphuric acid. It crystallises from methylic alcohol in yellowish needles which melt at 99°.

The *acetyl*-derivative of 2 : 3-hydroxynaphthoic acid melts at 176—177°, and its *methylic salt*, $\text{OAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{COOMe}$, crystallises in silky needles melting at 101°.

M. O. F.

Nitro-*β*-diazonaphthalenes. By F. GAESS and A. AMMELBURG (*Ber.*, 27, 2211—2215).—3'-*Nitronaphthalene-2:1-diazoxide* is obtained by boiling 1:3'-dinitro-2-diazonaphthalene with absolute alcohol, nitrous acid being eliminated; the same result is attained by agitating the solution of the diazo-derivative with ice. It forms golden-yellow plates which explode at 142—145°. Heated with hydrochloric acid, it yields a compound which crystallises in yellow needles, and melts at 178°. The diazoxide is easily reduced with tin

and hydrochloric acid, the stannochloride of the resulting base separating in colourless needles. The *acetyl*-derivative melts at 261°.

1'-Nitronaphthalene-2:1-diazoxide is obtained in a similar manner to the foregoing compound. It explodes with great violence at 155—156°.

An aqueous solution of 1-nitro-2-diazonaphthalene spontaneously undergoes change, with formation of naphthalene-2:1-diazoxide (Bamberger, this vol., i, 295); at the same time, a black crystalline compound is formed, which explodes at 115°. M. O. F.

Products of the Reduction of Alkylated Azo-colours of the Naphthalene Series. By O. N. WITT and H. v. HELMOLT (*Ber.*, 27, 2351—2357).—Of the two bases obtained by the reduction of ethoxyanilineazo- α -naphthol, one has been already described (*Abstr.*, 1892, 863). The remaining one forms a hydrochloride which dissolves readily in water, and crystallises in pale blue needles.

When ethoxyparatoluidineazo- α -naphthol is reduced, *ethoxyparatylorthodiamidonaphthalene*,

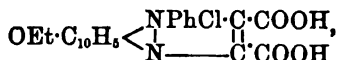
$\text{OEt} \cdot \text{C}_{10}\text{H}_7(\text{NH}_2) \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ [$\text{OEt} : \text{NH}_2 : \text{NH} \cdot \text{C}_6\text{H}_4\text{Me} = 1 : 3 : 4$],

is formed. It is deposited from petroleum in colourless needles, and melts at 118—119°. With benzile, it condenses to form *ethoxy-*

paratolynaphthostilbazonium chloride, $\text{OEt} \cdot \text{C}_{10}\text{H}_7 < \begin{array}{c} \text{NCl}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{CPh} \\ \text{N} \text{-----} \text{CPh} \end{array}$,

which, when heated at 130° with alcoholic ammonia, yields a substance belonging to the saffranine group.

Ethoxyphenylnaphthotarazonium chloride,



is obtained by warming ethoxydiamidophenylnaphthalene (*loc. cit.*) with sodium dihydroxytartrate in acetic acid solution on the water bath. The solutions in water and alcohol exhibit a brilliant green fluorescence, whilst the solution in strong sulphuric acid is dark red, becoming yellow on dilution. The homologue, *ethoxyparatolynaphthotarazonium chloride*, is obtained in an analogous manner; it forms hygroscopic, red needles, and hydrochloric acid causes a yellow *anhydride* to separate from the aqueous solution.

M. O. F.

Products of the Reduction of Alkylated Azo-colours of the Naphthalene Series. By O. N. WITT and A. BUNTROCK (*Ber.*, 27, 2358—2363).—*Phenetoilazo- α -ethoxynaphthalene*,



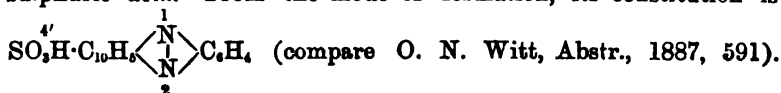
is prepared by heating phenolazo- α -naphthol with ethylic bromide and alcoholic potash. It is deposited from alcohol and from benzene in yellowish-red needles and prisms having a blue reflex; the melting point is 122—123°. *Phenolazo- α -ethoxynaphthalene*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_{10}\text{H}_7 \cdot \text{OEt}$, is formed by uniting with phenol the azo-compound obtained by diazotising paramido- α -naphthol. It melts

at 171°. *Phenetolazo- α -naphthol*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7\cdot\text{OH}$, is formed when diazotised phenetidine combines with α -naphthol. It melts at 168°, dissolves in dilute potash, and forms a bluish-violet solution with strong sulphuric acid.

When reduced, phenetolazo- α -ethoxynaphthalene yields *ethoxyamidonaphthylphenetidine*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7(\text{NH}_2)\cdot\text{OEt}$, which forms snowy needles melting at 103° and becoming red when exposed to the air. It condenses with benzile to form *diethoxyphenyl-naphthostilbazonium chloride*, $\text{OEt}\cdot\text{C}_{10}\text{H}_7\cdot\text{N}^+\text{Cl}(\text{C}_6\text{H}_4\cdot\text{OEt})\cdot\text{CPh}$. The action of alcoholic ammonia on the latter converts it into the *saffranine*, $\text{NH}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{N}^+\text{Cl}(\text{C}_6\text{H}_4\cdot\text{OEt})\cdot\text{CPh}$; this crystallises with $1\text{H}_2\text{O}$ in red needles, and melts at 150°. The *platinochloride* is red.

M. O. F.

Phenyl- β -naphthylaminesulphonic acids and Derived Azo-colours. By R. LESSER (*Ber.*, 27, 2363—2370).—When phenyl- β -naphthylamine is sulphonated, a mixture of phenyl-2-naphthylamine-4'-sulphonic acid and phenyl-2-naphthylamine-1'-sulphonic acid is formed (D.R.P. 53649). By the action of diazobenzenesulphonic acid on the former of these acids, a colouring matter is obtained which yields *phenonaphthazinesulphonic acid* when boiled with hydrochloric acid. This compound crystallises in lustrous, brown needles, and dissolves in water and alcohol, giving a red coloration with sulphuric acid. From the mode of formation, its constitution is



When fused with potash, the corresponding *eurhodole* is formed, the *potassium* salt of which is deposited from the melt in green crystals, dissolving in water to a red solution; from the latter, acetic acid liberates the free eurhodole in the form of a brown precipitate. The colouring matter obtained by the interaction of diazobenzene-sulphonic acid and phenyl-2-naphthylamine-4'-sulphonic acid, has the constitution $\text{NHPh}\cdot\text{C}_{10}\text{H}_7(\text{SO}_3\text{H})\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$. On reduction with stannous chloride and hydrochloric acid, the corresponding phenylnaphthalenediaminesulphonic acid is formed.

The colouring matter obtained in an analogous manner from phenyl-2-naphthylamine-1'-sulphonic acid, crystallises from hot water in fine, orange-coloured needles; on adding hydrochloric acid, the free acid separates in the form of a bluish-violet precipitate. It yields an acid on reduction, which, however, does not unite with benzile or dihydroxytartaric acid, and fails to give the characteristic green coloration with ferric chloride. With α -naphthol in the presence of potassium ferricyanide, it gives rise to an indo-phenol, and as this reaction is peculiar to paradiamine-derivatives of the benzene series, it is clear that the azo-group, in the first instance, must have entered the benzene ring, taking up the para-position to the naphthylamine residue. A comparison of the colour-

ing matter with the ammonium salt of phenylamidoazobenzene-sulphonic acid removes all doubt on this point. M. O. F.

Naphthylbenzenesulphonamides and Naphthyltoluenesulphonamides. By O. N. WITT and G. SCHMITT (*Ber.*, 27, 2370—2377; compare Hinsberg, *Abstr.*, 1891, 49).—These compounds are prepared by the action of benzenesulphonic or toluenesulphonic chloride on naphthylamine in the presence of caustic potash.

α-Naphthylbenzenesulphonamide, $\alpha\text{-C}_{10}\text{H}_7\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$, forms white, silky needles and melts at 166—167°. Like all these substances, it dissolves readily in caustic alkali, less easily in ammonia and alkali carbonates. The *β*-compound melts at 102—103°. *α*-Naphthyltolueneparasulphonamide, $\alpha\text{-C}_{10}\text{H}_7\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$, is obtained in transparent prisms, which melt at 157°; the *β*-compound melts at 133°.

These four compounds react with azo-derivatives; *α*-naphthyltolueneparasulphonamide and diazobenzenechloride yielding an orange colouring matter, which crystallises from alcohol in needles, and melts at 201°. It is identical with the substance obtained by the action of tolueneparasulphonic chloride on anilineazo-*α*-naphthylamine. Reduction leads to the formation of paranaphthylenediamine hydrochloride and tolueneparasulphonic chloride. Diazobenzenesulphonic acid and diazotised naphthionic acid also form dyes with *α*-naphthyltolueneparasulphonamide, whilst from diazobenzene chloride and *β*-naphthyltolueneparasulphonamide a red crystalline compound is obtained, which melts at 185°, and from diazobenzenesulphonic acid a substance crystallising in scarlet needles. Associated with the latter is a colourless substance, having

the constitution $\text{C}_{10}\text{H}_6\text{N} < \text{N} > \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K}$, formed by the oxidation of the colouring matter; when this salt is heated in a closed tube with fuming hydrochloric acid at 210°, the parent substance, phenylazimidonaphthalene is obtained. M. O. F.

Sulphonation in the Naphthalene Series. By O. DRESSER and R. KOTHE (*Ber.*, 27, 2137—2154).—In continuation of their investigations of this subject (this vol., i, 378), the authors have examined the action of fuming sulphuric acid on 1:1'-naphthylaminesulphonic acid, and find that, in addition to sulphonation, the amido- and sulphonic-groups in the peri-position condense, with elimination of water, the substances formed being sulphonic acids of the compound $\text{C}_{10}\text{H}_6 < \begin{smallmatrix} \text{NH} \\ \text{SO}_2 \end{smallmatrix}$, which the authors term *naphthosultam*, corresponding to the similar anhydride of 1:1'-amidonaphthol, to which Erdmann has given the name *naphthosultone*.

1:1'-Naphthosultam-2:4-disulphonic acid, $\text{SO}_2 > \text{C}_{10}\text{H}_4(\text{SO}_2\text{H})_2$, is obtained by heating the acid sodium salt of 1-naphthylamine-4:1'-disulphonic acid with fuming sulphuric acid at 80—90° for 5—6 hours. It is isolated in the usual manner as the sodium salt, $\text{C}_{10}\text{H}_4\text{NSO}_3\text{Na} + 8\frac{1}{2}\text{H}_2\text{O}$, which crystallises in large yellow plates,

and is extremely stable, undergoing no change when heated at 180° ; it is totally unacted on by nitrous acid, and dissolves readily in water, giving solutions showing a fluorescence similar to that of fluorescein. On adding hydrochloric acid, it yields the *disodium* salt, which crystallises in slender, colourless needles, the solution of which rapidly decomposes carbonates with evolution of carbonic anhydride. All attempts to convert the acid into the corresponding naphthylaminetrisulphonic acid have been unsuccessful, the naphthosultam ring being extremely stable.

When the above sodium salt is fused with soda at $180-190^{\circ}$, it is converted into the *sodium* salt of 1-amido-1'-naphthol-2 : 4-disulphonic acid, $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_4(\text{OH})(\text{NH}_2)\cdot\text{SO}_3\text{Na} + \text{H}_2\text{O}$, which crystallises in slender, colourless needles; its alkaline solution shows a green fluorescence. By the action of soda at 270° , the amido-group is also displaced by hydroxyl, with formation of 1 : 1'-dihydroxynaphthalenedisulphonic acid, whose *basic sodium salt*, $\text{ONa}\cdot\text{C}_{10}\text{H}_4(\text{OH})(\text{SO}_3\text{Na})_2 + 4\text{H}_2\text{O}$, crystallises in oblique prisms or plates having a greenish fluorescence. When heated with 20 per cent. fuming sulphuric acid at 160° , it is converted into 1 : 1'-dihydroxynaphthalene, proving that the above amidonaphtholdisulphonic acid is derived from 1 : 1'-amidonaphthol. That the sulphonic groups occupy the 2 : 4 positions is shown by the fact that the naphtholtrisulphonic acid obtained from naphthosultone (which, as will be proved later, is 1-naphthol-2 : 4 : 1'-trisulphonic acid) yields the same dihydroxynaphthalenedisulphonic acid on fusion with soda.

1-Naphthol-2 : 4 : 1'-trisulphonic acid is obtained by the action of fuming sulphuric acid on naphthosultone or on 1-naphthol-4 : 1'-disulphonic acid, and is isolated in the usual manner as the *sodium salt*, $\text{OH}\cdot\text{C}_{10}\text{H}_4(\text{SO}_3\text{Na})_3 + 1\frac{1}{2}\text{H}_2\text{O}$; this is a white, sandy, crystalline powder, which is coloured deep blue by ferric chloride in aqueous solution; its alkaline solutions show a deep green fluorescence. It is incapable of yielding azo-colours, which renders it probable that the third sulphonic group occupies the 2-position; this is shown conclusively by the fact that on treatment with sulphuric and nitric acid two of the sulphonic groups are displaced by nitro-groups, with formation of the colouring matter "brilliant yellow," which is 1-naphthol-2 : 4'-nitro-1'-sulphonic acid.

1 : 1'-Naphthosultamtrisulphonic acid, $\begin{array}{c} \text{SO}_3 \\ | \\ \text{NH} \end{array} > \text{C}_{10}\text{H}_3(\text{SO}_3\text{H})_2$, is obtained by treating 1-naphthylamine-3 : 3' : 1'-trisulphonic acid with fuming sulphuric acid at $70-80^{\circ}$; its *trisodium salt*, with $4\text{H}_2\text{O}$, crystallises in stellate groups of white, microscopic needles, and does not yield fluorescent solutions. The *tetrasodium salt*, with $4\text{H}_2\text{O}$, is an indistinctly crystalline, yellow mass, and the *barium salt* a yellow, crystalline powder. The formation of this acid shows that Armstrong and Wynne's sulphonation rule does not hold invariably, not only in the β -, but also in the α -series.

The additional sulphonic group probably occupies the 4-position, but this has not been proved with certainty; it is very readily eliminated by the action both of acids and of alkalis, with formation of 1-1'-

naphthosultam-3 : 3'-disulphonic acid, the *trisodium* salt of which, with $4\text{H}_2\text{O}$, crystallises in deep yellow, microscopic, rhombic plates, whilst the *disodium* salt forms spherical aggregates of colourless, microscopic needles. By fusion with soda, these salts are converted into 1 : 1'-amidonaphthol-3 : 3'-sulphonic acid (D.R.P. 69,722 and 67,062). Its acid *sodium* salt crystallises with $1\frac{1}{2}\text{H}_2\text{O}$ in asbestos-like aggregates of needles, the dilute solutions of which have a bluish-red fluorescence, which changes to reddish-violet on addition of alkalis.

When 2-naphthylamine-3' : 1'-disulphonic acid is heated with fuming sulphuric acid, a compound is obtained which no longer reacts with nitrous acid. No anhydro-ring similar to that of the naphthosultam derivatives is formed in this case, but the amido-group itself is sulphonated, the new compound being 3' : 1'-disulpho-naphthyl-2-sulphaminic acid, $\text{SO}_3\text{H}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6(\text{SO}_3\text{H})_3$; its *barium* salt crystallises with $10\text{H}_2\text{O}$ in orange-yellow needles, the *potassium* salt with $1\text{H}_2\text{O}$ in lustrous, orange-red needles, which on heating change to white, owing to the formation of sulphuric acid and the 3' : 1'-disulphonic acid. The same reaction readily takes place in solutions of the salts, especially in presence of acids. On further heating with fuming sulphuric acid, it undergoes a somewhat remarkable change, the sulphonic group migrating from the amido-group to the 1'-carbon atom, with formation of 2-naphthylamine-3 : 3' : 1'-trisulphonic acid (D.R.P. 27,378), the *acid potassium salt* of which crystallises with $1\frac{1}{2}\text{H}_2\text{O}$ in lustrous, white needles. H. G. C.

Anthraquinoneoxime. By E. SCHUNCK and L. MARCHLEWSKI (*Ber.*, 27, 2125—2127).—Anthraquinoneoxime, $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C:N}\cdot\text{OH}$, is readily obtained by Goldschmidt's method (*Abstr.*, 1884, 62), namely, heating anthraquinone with alcohol and hydroxylamine hydrochloride at 180° , and can be separated from the unaltered quinone by treating with alkalis, filtering, and reprecipitating the oxime with acid. It crystallises from dilute alcohol in pale yellow, matted, slender needles, commences to sublime at about 200° , and melts, when quickly heated, at 224° . It dissolves in alkalis, forming a reddish-brown solution, which is reprecipitated by carbonic anhydride; it is very stable towards hot concentrated sulphuric acid and towards Beckmann's mixture. It is not acted on by acetic chloride, but readily yields alkyl-derivatives, the *methyl-* and *ethyl-*derivatives crystallising in pale yellow, matted needles, and the *benzyl-*derivative in golden-yellow needles; these are all decomposed by hydriodic acid, and therefore contain the alkyl-group in combination with the oxygen.

The determination of the molecular weight in Beckmann's apparatus gave results agreeing with the above formula. H. G. C.

Oxidation of Cyclic Compounds. By G. WAGNER (*Ber.*, 27, 2270—2276; compare this vol., i, 469).—The author has oxidised French turpentine under the conditions previously described for menthene. The product is separated into two fractions boiling, under

14 mm. pressure, at 122—124° and 145—147° respectively; both these fractions are, however, mixtures. The fraction of higher boiling point gives analytical results agreeing with those required for pinene glycol, $C_{10}H_{18}O_2$. With carbanil, it yields a compound containing nitrogen, and when dehydrated by boiling with a few drops of hydrochloric acid, is converted into an oil which distils at 180—220°. The chief portion, however, distils at 180—190°, and when treated with bromine yields pinol bromide, melting at 92—93°; the higher fractions yield a small quantity of a crystalline oxime. Besides these dehydration products, a third is obtained which is not volatile with steam, crystallises in quadratic tablets, melts at 191—191·5°, and has the composition $C_{10}H_{16}O_2$, and is probably an α -glycolen. From the fraction boiling at 145—147°, the author has separated a compound melting at 76—78°, probably the pure glycol. This does not react with hydroxylamine or ammoniacal silver solution, although the fraction boiling at 145—147° does.

The fraction of lower boiling point (122—124°), $C_{10}H_{16}O_2$, has the composition of a ketoalcohol; it does not, however, react with carbanil. After remaining some time, it deposits crystals which melt at 97°, and yield a crystalline oxime, $C_{10}H_{16}(NOH)_2$, melting at 130°.

E. C. R.

Terpene-like Hydrocarbons in Petroleum. By R. ZALOZIECKI (*Ber.*, 27, 2081—2087).—A liquor was investigated that had been obtained in the purification of a mixture of crude petroleum from Potok and Wietirno. It was distilled with steam, then extracted with ether, and again distilled with superheated steam; the products were united and subjected to repeated fractionation, and the fractions, boiling respectively at 160—170° and 170—180°, were selected for further treatment. They were fractionated until they yielded products boiling respectively at 160—165° and 175—180°, and these were then treated separately with concentrated sulphuric acid. In this way, an oil (1) was obtained, partly polymerised but otherwise unaltered, and approximately of the composition C_nH_{2n-4} ; when treated with bromine, it yielded a tetrabromodihydrocumene melting at 186° (uncorr.) in the first case, and a tetrabromodihydrocymene, melting at 205°, in the second. On adding water to the sulphuric acid solution, an oil (2) separated out containing oxygen, and apparently a hydroxyl-derivative. Dissolved in the water there remained a sulphonic acid; the barium salt of this, when hydrolysed with hydrochloric acid, yielded (3) an oil, which, when nitrated, formed in the first case, trinitroparaethyltoluene melting at 92°, and in the second a trinitrocymene melting at 126° (uncorr.).

C. F. B.

Linalolene. By F. W. SEMMLER (*Ber.*, 27, 2520—2521).—*Linalolene*, $C_{10}H_{16}$, is obtained by reducing linaloöl with sodium and absolute alcohol, or better, by heating linaloöl with zinc dust in a sealed tube at 220—230°. It boils at 165—168°, has a sp. gr. at 20° of 0·7882, and a specific refractive power $n_D = 1·455$; from these values it follows that linalolene contains two doubly-linked carbon atoms, and therefore, like linaloöl, belongs to the olefine series of

2 u 2

compounds. This view receives further support from the fact that linalolene, like the hydrocarbons of the citral series, when heated on the water bath with concentrated sulphuric acid, undergoes isomeric transformation into a hydrocarbon (*cyclolinalolene*) boiling at 165—167°, having a specific gravity at 17° of 0.8112, and a specific refractive power $n_D = 1.4602$, and therefore containing but one doubly-linked carbon atom.

A. R. L.

Action of Sulphuric acid on Camphene. By G. BOUCHARDAT and J. LAFONT (*Compt. rend.*, 119, 85—87).—Concentrated sulphuric acid acts energetically on camphene, but the action is less violent than with terebenthenes and terpenes, the development of heat is less, and the products are different.

When racemic camphene is mixed, drop by drop, with one-tenth its weight of monohydrated sulphuric acid, the vessel being cooled, a homogeneous, almost colourless liquid is formed, without any separation of brown resinous acid substances. The chief product is the ether of inactive camphene borneol, $C_{10}H_{18}O_2$. It forms long, channelled, rhombohedral prisms, which melt at 90—91°, and boil at 322° under normal pressure, without undergoing any notable decomposition. Bromine yields an unstable additive product, and phosphorus pentachloride is without action on solutions in light petroleum at the ordinary temperature. Hydrochloric acid saturated at 0° has no action on the compound at 100°, but at 150° converts it into camphene hydrochloride. Fuming nitric acid attacks it in the cold with formation of camphor, and an acetic acid solution of chromic anhydride likewise oxidises it to camphor. Acetic anhydride is almost without action, but at 200° a small quantity of camphene is formed.

The other products are borneolsulphonic acid, which, by hydrolysis, yields the borneol of inactive camphene, and a small quantity of polymerides of camphene, the most abundant being $C_{40}H_{72}$.

The same ether of the borneol is obtained in small quantity by treating the camphene with a mixture of glacial acetic acid and sulphuric acid, but in this case the principal product is the borneol acetate of camphene borneol.

C. H. B.

Pine Tar. By A. RENARD (*Compt. rend.*, 119, 165—166).—Pine tar of sp. gr. 1.054 was found to contain water, 3.5; hydrocarbons boiling below 300°, 12.0; hydrocarbons boiling between 300° and 360°, 45.0; phenols, 18.0; resin rich in retene, 21.5 = 100.00°. In order to isolate the terebenthene, the fraction boiling between 160° and 180° is boiled with sodium to remove oxygen compounds, and is then fractionated. The terebenthene boils at 171—174°; sp. gr. at 0° = 0.866; rotatory power, $[\alpha]_D = 19.1^\circ$; refractive index, 1.4785; vapour density, 4.6. It absorbs oxygen more rapidly than ordinary terebenthene. With bromine, in presence of carbon bisulphide, it yields an unstable additive product, $C_{10}H_{16}Br_2$, and with bromine alone it yields a tetra-substitution derivative, $C_{10}H_{12}Br_4$, an oily liquid, which after some time partially crystallises. The dihydrochloride melts at 49.5°, and is obtained by the action of hydrogen chloride on the

terebenthene alone, or in ethereal solution. When the terebenthene is mixed with ordinary sulphuric acid, it yields a polymeride boiling above 300° , cymene, and a small quantity of cymene hexahydride, $C_{10}H_{20}$, which boils at about 170° , and is not attacked by bromine or fuming nitric acid at the ordinary temperature. C. H. B.

Constitution of Camphor. By J. BREDT (*Ber.*, **27**, 2092—2099).—It is known that when camphor is oxidised the product consists, to the extent of about two-thirds, of camphoric and camphoronic acids. The author has now shown that the remainder contains oxalic, dimethylmalonic, succinic, and trimethylsuccinic acids; the method adopted was to convert the mixture of acids into a mixture of their ethylic salts, and to fractionate this under diminished pressure. The formation of these acids is further evidence in favour of the author's formula for camphor (this vol., i, 141). In the rest of the paper he attempts to refute the objections of Aschan (this vol., i, 422), and assigns the formula $COOH \cdot CMe < \begin{smallmatrix} CH_2 \cdot CH_2 \\ -CMe_2- \end{smallmatrix} > C \cdot COOH$ to isocamphanic acid, the relation of which to various other acids obtained from camphor is discussed. C. F. B.

Relation between the Rotatory Power of Camphor and the Molecular Weights of certain Solvents. By MOREAU (*J. Pharm.*, [5], **30**, 14—19).—Tables showing the rotatory power of camphor dissolved in aromatic hydrocarbons, alcohols of the fatty series, acids of the fatty series, and alkyl salts of fatty acids, are given. The author draws the following conclusions from the figures. (1) The rotatory power of camphor in solution increases with the concentration of the solution. (2) The rotatory power suffers no alteration with the lapse of time. (3) Solutions in isomeric modifications of the same solvent show the same rotatory power. (4) In an homologous series of solvents, the influence of concentration on rotatory power is the same; the rotatory power increases with the molecular weight of the solvent proportionally to the increase in the molecular weight. (5) The results indicate that the solvents form true combinations with the camphor, and it is not improbable that such a combination is effected at the summit of a tetrahedron adjacent to the radicle, C_3H_7 . A. G. B.

Tautomerism of Oxymethylene Compounds. By O. ASCHAN and J. W. BRÜHL (*Ber.*, **27**, 2398—2404).—Formylbromocamphor, $C_9H_{14} < \begin{smallmatrix} CBr \cdot CHO \\ CO \end{smallmatrix}$, is prepared by the direct bromination of oxymethylenecamphor; it crystallises in four-sided, white leaflets melting at 44° , and is not acted on by bromine. It dissolves in concentrated sodium hydrogen sulphite, and is not precipitated from the solution by acids; with phenylhydrazine, it yields a substance which contains no bromine, and crystallises in hemihedral monosymmetric crystals melting at 124 — 125° . Formylbromocamphor is converted into bromocamphor by potash.

Methoxymethylenecamphor on bromination yields a crystalline

additive *product*, $C_{15}H_{18}Br_2O_2$, which melts at 78° ; it evolves methylic bromide and hydrogen bromide in a vacuum giving formylbromocamphor. A similar unstable additive *product* is obtained from ethoxymethylenecamphor; it spontaneously decomposes into ethylic bromide and formylbromocamphor.

The above bromo-derivatives seem to be tautomeric in constitution with oxymethylenecamphor. W. J. P.

Camphorpinacene. By E. BECKMANN (*Ber.*, 27, 2348—2350; compare this vol., ii, 434).—This substance is formed as a bye-product in the conversion of camphor into borneol by the prolonged action of sodium in ethereal solution (*Ber.*, 22, 912). The *chloride*, $C_{20}H_{31}Cl$, which melts at 75° , is obtained by the action of hydrochloric acid on the pinacene, and, like that substance, it is optically active, having $[\alpha]_D = +45$; it is also formed when acetic chloride or phosphorus oxychloride acts on the pinacene. Similarly, hydrobromic acid gives rise to the *bromide*, which melts at 103° . The *methylic ether*, $C_{21}H_{34}O$, is obtained by the action of methylic alcohol on these compounds; it melts at 98° , and has $[\alpha]_D = -80^\circ$. The *ethylic ether*, $C_{22}H_{36}O$, melts at 58° , and the *propylic ether*, $C_{23}H_{38}O$, at 86° . The *acetate* melts at 74° . If the chloride or bromide is mixed with acetic acid and an alcohol in which sodium has been dissolved, the ether of the alcohol employed is produced. These ethers are isomeric with those already described, but are not identical. The *methylic ether* melts at 67° , and has $[\alpha]_D = -133^\circ$. The *ethylic ether* melts at 58° , whilst the *acetate*, obtained by adding zinc dust to a mixture of the halogen compound with ether and glacial acetic acid, melts at 109° .

The halogen in the chloride and bromide may be displaced by hydroxyl on treatment with moist silver oxide; the same result is produced by caustic potash or boiling water in the presence of zinc dust. The *hydroxy*-derivative obtained in this way melts at 120° , and is converted into the original chloride by the action of acetic chloride or hydrochloric acid. When treated with cold glacial acetic acid, it yields the acetate, which melts at 109° , the modification of lower melting point being formed when boiling acid is used. Phenyl isocyanate gives rise to a *compound*, $C_{27}H_{39}O_2N$, which melts at 161° .

When hydrogen chloride is eliminated from the chloride by the action of sodium carbonate at 150° , a *hydrocarbon*, $C_{20}H_{30}$, is formed, melting at 56° . It is unsaturated, and yields the chloride, melting at 75° , when treated with hydrogen chloride; the *nitrosochloride* melts at 150° , and the *dibromide* at 157° , the hydrocarbon being regenerated when zinc dust acts on the dibromide dissolved in acetone. Moist silver oxide converts the dibromide into the corresponding *glycol*, which melts at 150° . A *hydrocarbon*, $C_{20}H_{32}$, melting at 98° , is the final product of the action of hydrogen iodide on the hydrocarbon, $C_{20}H_{30}$, and it is also formed in the same way from the pinacene or its methylic ether. This substance, when treated with bromine, yields the dibromide already described. M. O. F.

Oxidation of Camphoric acid. By L. BALBIANO (*Ber.*, 27, 2133—2137).—The author has repeated his experiments (*Abstr.*, 1893,

i, 174) on the oxidation of camphoric acid on a larger scale, and finds that the bibasic acid obtained has the composition $C_8H_{12}O_6$, and its calcium salt the formula $C_8H_{10}O_6Ca + 2H_2O$. The dimethylic salt, $C_8H_{10}O(COOMe)_2$, is a thick, colourless liquid, which boils at $164-165^\circ$ (corr.), has a sp. gr. of 1.145 at $15^\circ/15^\circ$, a pleasant, resinous odour, and biting taste. The acid contains the hydroxyl group, as it readily yields *acetyl*- and *benzoyl*-derivatives, both of which are colourless oils, boiling respectively at $165-166^\circ$ under 22 mm. pressure, and at 200° under 20 mm. pressure.

When reduced by a mixture of hydriodic acid and red phosphorus, it yields a mixture of two acids, $C_8H_{12}O_4$ and $C_8H_{14}O_4$, which are separated by the difference in the solubilities of their calcium salts, that of the former being almost insoluble in boiling water, although soluble in cold water. The acid, $C_8H_{14}O_4$, crystallises from water at 80° , in hard, white, prismatic crystals melting at $88-89^\circ$; its composition is that of a dimethyladipic acid, but it is not identical with Zelinsky's α,α -dimethyladipic acid. The acid, $C_8H_{12}O_4$, crystallises in flattened prisms melting at $163-164^\circ$ (corr.), and in composition and melting point resembles Perkin's *cis*-hexahydroisophthalic acid (Trans., 1891, 798); it is not, however, identical with that compound, as it is not converted into an anhydride by boiling with acetic chloride. By the action of potassium permanganate, it is reconverted into the acid, $C_8H_{12}O_4$. H. G. C.

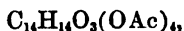
Action of Alkalis on Bromocamphoric Anhydride. By O. ASCHAN (*Ber.*, 27, 2112-2116).—Attempts to obtain a bromo-derivative of isocamphoric acid (this vol., i, 538) have not led to the desired result, the product being chiefly bromocamphoric anhydride. In one case, a small quantity of a brominated acid was obtained, which crystallises in needles, and melts at 196° , but the quantity was insufficient for analysis. When treated with alkalis, it is converted into an oily, unsaturated acid, which closely resembles lauranolic acid (*Absr.*, 1885, 669). An acid, apparently identical with the latter, is also obtained, together with camphanic acid, by the action of alkalis on bromocamphoric anhydride, as already observed by Fittig and Woringer; the author finds that, under suitable conditions, the yield of the unsaturated acid may rise as high as 17 per cent. The acid unites very readily with bromine, but hydrogen bromide is quickly evolved, and the product, after treatment with soda and recrystallisation from acetic acid, crystallises in large, pointed needles melting at $183-184^\circ$. It behaves as a brominated lactone, and is immediately oxidised by potassium permanganate, with formation of an acid soluble in water and ether; these products are being further investigated. The formation of an unsaturated acid from bromocamphoric acid, with evolution of carbonic anhydride and hydrogen bromide, is analogous to the decomposition of the β -bromo-fatty acids, and it therefore appears probable that in bromocamphoric acid the bromine atom is in the β -position to one of the carboxyl groups; Fittig, on other grounds, has already shown that the same atom is probably in the γ -position to the other carboxyl group. H. G. C.

Picein, a Glucoside from the Leaves of *Pinus picea*. By TANRET (*Compt. rend.*, 119, 80—83).—The finely chopped leaves of *Pinus picea* are treated with boiling water containing 5 grams of sodium hydrogen carbonate per kilo. of leaves, boiled for a few minutes, and allowed to macerate for 24 hours. The liquid is then precipitated successively with basic lead acetate and ammoniacal lead acetate. The latter precipitate is decomposed by sulphuric acid, the liquid filtered, neutralised with magnesium oxide, and evaporated to a syrup, which, whilst still warm, is mixed with one-third its weight of magnesium sulphate, and extracted with ethylic acetate. The latter is distilled, and the residue after being purified by treatment with absolute alcohol, is finally crystallised from boiling absolute alcohol or from boiling water.

Picein, $C_{14}H_{18}O_7$, whether anhydrous or hydrated, crystallises in silky, prismatic needles, with a bitter taste, soluble in 50 parts of water at 15° , and in an equal weight of boiling water; it is only slightly soluble in cold absolute alcohol, much more so in boiling alcohol, and insoluble in ether or chloroform. It is laevogyrate, $[\alpha]_D = -84^\circ$ in aqueous solution, and -78° in alcoholic solution. Anhydrous picein melts at 194° ; the hydrate contains $1H_2O$.

Under the influence of emulsin, picein reacts with 1 mol. H_2O , and yields glucose and piceol in molecular proportion; dilute acids induce the same change, and the piceol crystallises equally well in both cases. Picein dissolves in concentrated sulphuric acid, with production of only a very faint brownish tinge, a reaction which distinguishes it from coniferin. It is not precipitated either by tannin, or by basic lead acetate, but with ammoniacal lead acetate it yields a precipitate of the composition $C_{14}H_{14}PbO_7$. It is also precipitated by magnesium sulphate, but does not combine with it. Although very slightly soluble in cold water, it dissolves readily in presence of the amorphous glucosides which accompany it in the leaves, and which seem to be its natural solvent.

When heated with acetic anhydride in presence of a small quantity of zinc chloride, picein yields a crystallisable tetracetate,



which melts at 170° , and is soluble in ether.

Piceol, $C_8H_8O_2$, melts at 109° , and dissolves in 100 parts of water at 15° , and in 14 parts of boiling water. With ferric chloride, it gives a violet coloration. It dissolves in solutions of alkali carbonates without liberation of carbonic anhydride, and with alkali hydroxides it forms crystallisable compounds, which are decomposed by carbonic anhydride, but not by water. It also forms an acetate and a benzoate, and generally behaves like a monhydric phenol. The barium compound has the composition $BaO(C_8H_7O_2)_2$, and the benzoate, which melts at 134° , has the composition $C_8H_7O \cdot OBz$. C. H. B.

Crystalline Form of Tetramethylbrazilin. By A. STENGEL (*Momatsk.*, 15, 269—272; compare Schall, this vol, i, 257; Herzig, *ib.*, 341).—Tetramethylbrazilin crystallises in monosymmetric plates;

$a : b : c = 0.9392 : 1 : 0.9782$. $\beta = 90^\circ 23\frac{1}{2}'$. It is crystallographically very closely related to trimethylbraziliu. W. J. P.

γ -Amidovaleric acid and Methylpyrrolidone. By L. SENFTER and J. TAFEL (*Ber.*, **27**, 2313—2314).—*Benzoyl- γ -amidovaleric acid* forms white, interlacing crystals, melts at 132° , and when heated at higher temperatures loses the elements of water.

1-Acetyl-2-methylpyrrolidone is obtained by boiling methylpyrrolidone with acetic anhydride in a reflux apparatus. It is a pale yellow, limpid oil, boils at 224 — 226° , does not solidify at -17° , and has an odour resembling that of peppermint.

1:2-Dimethylpyrrolidone is obtained by heating methylpyrrolidone with methylic iodide for 12 hours, in a sealed tube, at 150° . It is a colourless oil, having a faint odour, boils at 215 — 217° under 743 mm. pressure, and does not solidify when cooled. E. C. R.

Action of Piperidine on Ethylic Acetoacetate. By F. B. AHRENS (*Ber.*, **27**, 2088—2089).—By mixing these two substances, and finally heating the mixture, acetopiperidine, $C_8H_{10}Ac$, is obtained. It is a colourless oil, boils at 224° , or under 30—40 mm. pressure at 135 — 137° , and is decomposed by heating with acids or alkalis, or when its hydrochloride is heated, the products being piperidine and acetic acid. The hygroscopic *hydrochloride* melts at 95° , the deliquescent *hydrobromide* at 131 — 133 , the red *platinochloride* at 107 — 109° , and the *aurochloride* at 67 — 68° . C. F. B.

Action of Chloroform and Potash on Piperidine. By F. B. AHRENS (*Ber.*, **27**, 2090—2091).—When caustic potash is added to a mixture of chloroform and piperidine, and the whole finally warmed on the water bath, formylpiperidine, $C_8H_{10}CHO$, is obtained. This has the properties ascribed to it by Wallach and Lehmann (*Annalen*, **237**, 252) and Lachowicz (*Monatsh.*, **9**, 700). C. F. B.

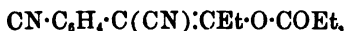
β -Bromoquinoline and γ -Bromoquinoline. By A. CLAUS and H. HOWITZ (*J. pr. Chem.*, [2], **50**, 232—239).—When kynurine is heated with phosphoric bromide, even with only a slight excess, and for a short time, and not above 120 — 130° , the hydroxyl is not simply replaced by bromine. The main product is colourless *3':4'-dibromoquinoline*, melting at 82° , which, when heated at 200° with concentrated hydrochloric acid, yields colourless *3':4'-dihydroxyquinoline*, melting at about 340° ; some *monobromoquinoline* is, however, obtained. This melts at about 25° , and when heated to 270° , begins to boil, and is transformed into the above-mentioned dibromoderivative. It is readily soluble in cold dilute acids, is reconverted into kynurine when it is heated with hydrochloric acid at 150° , and cannot be converted into bromocarbostyryl in the usual way. It readily unites with methylic iodide at 60 — 80° , forming a yellow compound that melts at 265 — 270° , and is not oxidised by alkaline ferricyanide to a crystalline quinoline. It has thus none of the properties of the monobromoquinoline obtained from quinoline by direct substitution; it can, however, be shown to be a *4'*-derivative in the

following manner. Cinchoninic acid is known to be a 4'-carboxy-compound; when its ethylic salt is treated with concentrated aqueous ammonia at the ordinary temperature, colourless *cinchoninamide*, melting at 181°, is formed. By carefully oxidising this with a slight deficiency of bromine in alkaline solution, 4'-*amidoquinoline*, melting at 69—70°, is obtained (together with some substance identical with the 3'-bromo-4'-*amidoquinoline* mentioned below). This 4'-*amidoquinoline* can be diazotised in sulphuric acid hydrate solution; when the product is poured into cuprous bromide solution, 4'-*bromoquinoline* is formed, identical with the *bromoquinoline* obtained from *kynurine*; if the product is poured into water, *kynurine* itself is produced.

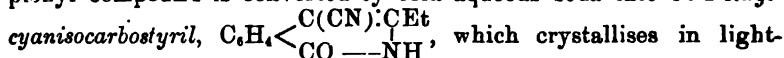
If an attempt is made to diazotise 4'-*amidoquinoline* in hydrochloric acid solution, a *chloroquinoline* is formed, identical with that obtained by the action of phosphoric chloride on *kynurine*. If the attempt is made in hydrobromic acid solution, substitution takes place, and 3'-*bromo-4'-amidoquinoline* is formed. This melts at 203°, and sublimes unchanged. It can be diazotised in sulphuric acid hydrate solution, and, when the product is poured into alcohol, 3'-*bromoquinoline* is formed; this is found to be identical with the *bromoquinoline* obtained from *quinoline* by direct substitution.

The direct action of bromine on *quinoline* thus gives rise, not, as hitherto supposed, to 4'-, but to 3'-*bromoquinoline*. C. F. B.

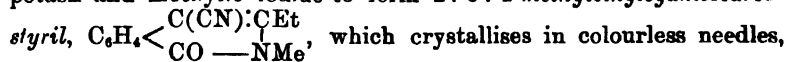
Synthesis of 3-Ethylisoquinoline. By F. DAMEROW (*Ber.*, 27, 2232—2243; compare this vol., i, 279).—When orthocyanobenzyl cyanide is heated with propionic anhydride, it is converted into *ψ-dipropionylorthocyanobenzyl cyanide*,



which crystallises in slender, silky needles, melting at 135·5°, together with a substance of higher melting point. The *ψ-dipropionyl* compound is converted by cold aqueous soda into 3:4-*ethylcyanisocarbostryl*,

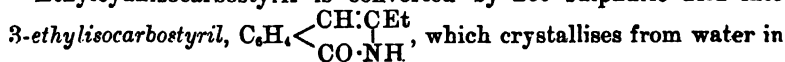


brown, flat rhombic tablets melting at 261—262°. This substance is insoluble in aqueous acids, sparingly soluble in water, and insoluble in ammonia, but dissolves in boiling aqueous soda. It reacts with potash and methylic iodide to form 2:3:4-*methylethylcyanisocarbostryl*,



and melts at 135—136°. The corresponding ethylic derivative could not be obtained.

Ethylcyanisocarbostryl is converted by hot sulphuric acid into 3-*ethylisocarbostryl*,



colourless, microscopic tablets melting at 140—141°. A better yield is obtained by the substitution of phosphoric acid for the sulphuric acid. *Methylethylcyanisocarbostryl* undergoes a similar change,

and is converted into 2:3-methylethylisocarbostyryl, which forms splendid, colourless needles melting at 113—113.5°.

Ethylisocarbostyryl is converted by phosphorus oxychloride into 1:3-chlorethylisoquinoline, $C_6H_4 \begin{smallmatrix} CH:C \\ CCl:N \end{smallmatrix} Et$, which forms colourless, concentrically-arranged groups of needles, melts at 24°, and boils at 288° under a pressure of 751.5 mm.; it has faintly basic properties, but is precipitated from solution in hydrochloric acid by water. The *picrate* melts at 113—114°, the *platinochloride* forms small, flesh-coloured needles, which decompose at 290—300°, whilst the *aurochloride* melts at 160—161.

3-Ethylisoquinoline, $C_6H_4 \begin{smallmatrix} CH:C \\ CH:N \end{smallmatrix} Et$, may be prepared by reducing chlorethylisoquinoline with hydriodic acid, or by distilling 3-ethylisocarbostyryl with zinc dust. It is a colourless, very refractive liquid, boils at 255—256°, and has a strong odour of quinoline. The *picrate* forms yellow, rhombic tablets melting at 171—172°, the *platinochloride* melts and decomposes at 180°, and the *aurochloride* melts at 115—117°.

1:3-Methoxyethylisoquinoline, $C_6H_4 \begin{smallmatrix} CH:C \\ C(OMe) \end{smallmatrix} Et \rangle N$, is obtained by the action of sodium methoxide on chlorethylisoquinoline. It is a colourless, very refractive, mobile liquid, boils at 266—267°, and has a pleasant odour. The *picrate* melts at 129°, whilst the *platinochloride* decomposes at 167°. *Ethoxyethylisoquinoline* boils at 274°; the *picrate* melts at 148°, and the *platinochloride* decomposes at 176°. *Phenoxyethylisoquinoline* is a brown oil. The *picrate* is a yellow, crystalline powder melting at 135—136°. When treated with bromine, this base forms an unstable *perbromide*, which gradually passes into 1-bromophenoxy-3-ethylisoquinoline; this crystallises from dilute alcohol in colourless needles melting at 58—59°.

The substance of higher melting point obtained in the preparation of dipropionylorthocyanobenzyl cyanide is also obtained in small amount when the latter is submitted to the action of alkalis. It forms yellow crystals melting and decomposing at 260—261°, and is a polymeride of orthocyanobenzyl cyanide, its molecular formula being $(C_6H_4.N_2)_2$.

Ortho-a-dicyano-β-ethoxybutenylbenzene, $CN \cdot C_6H_4 \cdot C(CN) : CEt : OEt$, is obtained when dipropionylcyanobenzyl cyanide is acted on with alkali in the presence of alcohol. It forms colourless prisms, melts, after previously softening, at 58°, and is readily soluble in the usual solvents. Hydrochloric acid at 100° converts it into ethylic chloride and cyanethylisocarbostyryl. When methylic alcohol is employed, the corresponding *methoxy*-derivative is obtained; this forms colourless, rhombic tablets, and melts at 66—67°. A. H.

Oxazolines and Thiazolines of the Anisic acid Series. By P. REHLÄNDER (*Ber.*, 27, 2154—2161).—The bromalkylated anisamides necessary for the preparation of the oxazolines and thiazolines of this series are obtained by treating anisic chloride with brom-

alkylamines and aqueous soda at a temperature not exceeding 30°. *β*-Bromethylanisamide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, crystallises in colourless needles melting at 162°; *γ*-bromopropylanisamide,



in needles melting at 77·5°; and *β*-bromopropylanisamide,



in slender needles melting at 85°.

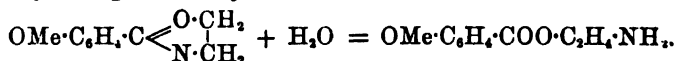
To prepare the oxazolines, the alkylanisamides are dissolved in warm alcohol and treated with the requisite quantity of alcoholic potash.

Mesoparamethoxyphenyloxazoline, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{O} \\ \parallel \\ \text{N} \end{smallmatrix}\text{C}_6\text{H}_4$, crystallises from light petroleum in colourless plates melting at 63°, the *picrate* melts at 192°, the *aurochloride*, $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}\cdot\text{AuCl}_4$, at 164—166°. *Meso-*

paramethoxyphenylpentoxazoline, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{O}\cdot\text{CH}_2 \\ \parallel \\ \text{N}\cdot\text{CH}_2 \end{smallmatrix}\text{CH}_2$, is an oil,

and yields a *hydrobromide*, which, after crystallisation from alcohol, melts at 143°; the *picrate* melts at 131—133°, and the *platinochloride* at 187—188° with decomposition. *β*-Methylmesoparamethoxyphenyloxazoline, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{O}\cdot\text{CHMe} \\ \parallel \\ \text{N}\cdot\text{CH}_2 \end{smallmatrix}$, is also an oil; the *hydrobromide* melts at 179°, the *picrate* at 177°, and the *platinochloride* at 201°.

The bromalkylanisamides are also converted by boiling with water into the hydrobromides of the oxazolines, but these again take up water, yielding *amidoalkylic anisates*, thus—

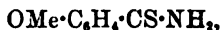


β-Amidoethylic anisate crystallises in colourless plates melting at 52°; the *hydrobromide* in needles melting at 199—200°; the *picrate* melts at 173°; and the *platinochloride* at 217°. The *hydrobromide* of *γ*-amidopropylic anisate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COO}\cdot[\text{CH}_2]_3\cdot\text{NH}_2\cdot\text{HBr}$, melts at 95—97°; the *picrate* at 161—162°; and the *platinochloride* at 205°. The *hydrobromide* of *β*-amidopropylic anisate,



melts at 164—167°; the *picrate* at 189°; and the *platinochloride* at 213°.

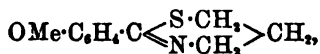
The thioanisamide necessary for the preparation of the thiazolines was obtained by distilling anisic acid with lead thiocyanate, and treating the anisonitrile thus obtained with alcoholic ammonium sulphide at 100°. *Anisonitrile*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$, boils at 245—255°, and crystallises at the ordinary temperature; and *thioanisumide*,



crystallises from hot water in yellow plates melting at 148—149°. When boiled with ethylenic bromide, it is converted into *mesopara-*

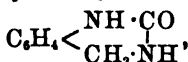
methoxyphenylthiazoline, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{S}\cdot\text{CH}_2 \\ \parallel \\ \text{N}\cdot\text{CH}_2 \end{smallmatrix}$, which crystallises from

light petroleum in well-developed, yellowish crystals melting at 54.5° ; its *picrate* melts at 187° ; and its *platinochloride* at 213° with decomposition. *Mesoparamethoxyphenylpenthiazoline*,

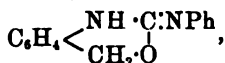


obtained by boiling thioanisamide with trimethylene chlorobromide, crystallises from light petroleum in well-developed, colourless crystals melting at 46° ; its *picrate* melts at $107-108^\circ$; and its *platinochloride* at 204° with decomposition. H. G. C.

Constitution of Söderbaum and Widman's Phenylldihydroketometadiazines and Phenylldihydrothiometadiazines. By C. PAAL and L. VANVOLXEM (*Ber.*, 27, 2413-2427).—Busch (*Abstr.*, 1892, 1495) obtained phenyltetrahydroketoquinazoline,



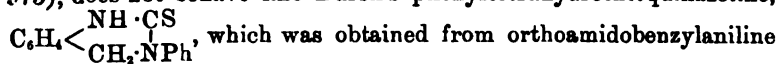
melting at 189° , by the action of carbonyl chloride on orthoamidobenzylaniline. Now Söderbaum and Widman (*Abstr.*, 1890, 178) had given this formula, with the name "benzophendihydroketometadiazine," to the compound melting at $145-146^\circ$, obtained from orthoamidobenzyl alcohol and phenylcarbimide. This compound, however, is now shown to exhibit none of the reactions of Busch's ketoquinazoline; it must, therefore, have the alternative formula



and the name phenylimidocoumazone is assigned to it.

Phenylimidocoumazone is a basic substance; the *hydrochloride* melts at 102° . It is reduced by sodium in alcoholic solution to aniline and orthotoluidine. With acetic and benzoic chlorides, it forms additive products melting at 119° and 117° respectively; and it also yields oily additive products with the corresponding acid anhydrides. When boiled with aniline, it yields Busch's phenyltetrahydroketoquinazoline, together with some symmetrical diphenylcarbamide; with paratoluidine, it reacts in an analogous manner. It behaves thus in an entirely different manner from phenyltetrahydroketoquinazoline.

In a similar way, it is shown that Söderbaum and Widman's benzophenylldihydrothiometadiazine, melting at 197° (obtained from orthoamidobenzyl alcohol and phenylthiocarbimide, *Abstr.*, 1889, 973), does not behave like Busch's phenyltetrahydrothioquinazoline,



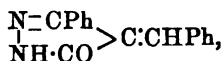
and carbon bisulphide in alcoholic potash solution, and melts at about 245° . To the former compound the formula $\text{C}_6\text{H}_4 < \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{NPh} \\ \text{CH}_2 \cdot \text{S} \end{array}$,

and the name *phenylimidocoumothiazone*, are assigned. This compound has basic properties, is reduced by sodium in alcoholic solution

to aniline and orthotoluidine, yields additive compounds with acetic and benzoic chlorides (melting, in the latter case, at 140°), and does not react with aromatic amines. C. F. B.

Synthesis of Coumothiazone Derivatives. By C. PAAL and O. COMMERELL (*Ber.*, 27, 2427—2433).—When orthoamidobenzyl alcohol is boiled with carbon bisulphide in alcoholic potash solution, yellowish *thiocoumothiazone*, $C_6H_4 \begin{smallmatrix} NH \cdot CS \\ \diagdown \quad \diagup \\ CH_2 \cdot S \end{smallmatrix}$ or $C_6H_4 \begin{smallmatrix} N = C \cdot SH \\ \diagdown \quad \diagup \\ CH_2 \cdot S \end{smallmatrix}$, melting at 166° , is formed. It has acid properties, forming crystallised *potassium* and *sodium salts*, and, when boiled with methylic iodide in alcoholic potash solution, it yields a yellowish, *methyl-derivative* melting at 73° . In boiling alcoholic solution, it is reduced by sodium to orthotoluidine. When boiled with aniline, it yields phenylimidocoumothiazone, $C_6H_4 \begin{smallmatrix} NH \cdot C \cdot NPh \\ \diagdown \quad \diagup \\ CH_2 \cdot S \end{smallmatrix}$, and some phenyl-tetrahydrothioquinazoline, $C_6H_4 \begin{smallmatrix} NH \cdot CS \\ \diagdown \quad \diagup \\ CH_2 \cdot NPh \end{smallmatrix}$ (compare preceding abstract). With paratoluidine, it acts in an analogous fashion, yielding *paratolylimidocoumothiazone*, melting at 187° , and *paratolyl-tetrahydrothioquinazoline*. C. F. B.

Pyrazolone and Isopyrazolone. By R. v. ROTHENBURG (*J. pr. Chem.*, [2], 50, 227—231).—The author denies that Ruhemann can have isolated isopyrazolone (this vol., i, 476); the substance obtained by the latter must have been a polymeride of pyrazolone. Pyrazolone and isopyrazolone are, he reasserts, tautomeric, and isomeric only in their derivatives. In proof of this he states that 3-phenylpyrazolone acts both as a pyrazolone- and as an isopyrazolone-derivative. As a pyrazolone derivative $\begin{smallmatrix} N = CPh \\ | \\ NH \cdot CO \end{smallmatrix} > CH_2$, in that it yields with benzaldehyde a reddish-brown 4-benzal-derivative,



not melting below 250° ; and with nitrous acid a red 4-isonitroso-derivative, melting at 184° , the purple-red silver salt of which explodes at 242° . As an isopyrazolone derivative, $\begin{smallmatrix} NH \cdot CPh \\ | \\ NH \cdot CO \end{smallmatrix} > CH$, in that it

yields with excess of acetic anhydride a 1 : 2-diacetyl derivative, $\begin{smallmatrix} NAc \cdot CPh \\ | \\ NAc \cdot CO \end{smallmatrix} > CH$, melting at 86° , and its 4-azobenzene derivative

yields with benzaldehyde a red compound $CHPh < \begin{smallmatrix} N \cdot CPh \\ | \\ N - CO \end{smallmatrix} > CH$,

melting at 131° . Further, 3 : 4-dimethylpyrazolone yields, with acetic anhydride, 1 : 2-diacetyl-3 : 4-dimethylpyrazolone, melting at 44° ; whilst 3 : 4 : 4-trimethylpyrazolone, in which the movable hydrogen that is the cause of the tautomerism is replaced by methyl, yields only a 1-acetyl-3 : 4 : 4-trimethylpyrazolone. C. F. B.

Phenylisoxazoloneimide. By R. v. ROTHENBURG (*J. pr. Chem.*, 50, 231).—A question of priority. The author admits that Burns (*Abstr.*, 1893, i, 315) had, before himself, assigned the right constitution to phenylisoxazoloneimide, and apologises for having overlooked his work.
C. F. B.

The Aldehydine Reaction. By O. HINSBERG and F. FUNCKE (*Ber.*, 27, 2187—2193).—Phenyleneamidines (the aldehydines of Ladenburg) have already been shown to result from the action of aldehydes on orthodiamines (*Abstr.*, 1887, 817).

Acetaldehydine, $C_6H_4 < \begin{smallmatrix} NEt \\ N \end{smallmatrix} > CMe$, is obtained from acetaldehyde and orthophenylenediamine, or by heating ethylorthophenylenediamine with glacial acetic acid at 170° ; it is a colourless oil, which boils at 257° (60 mm.), and becomes red in the air (compare Hempel, *Abstr.*, 1890, 612). The *hydriodide*, $C_{10}H_{12}N_2 \cdot HI + H_2O$, loses water at 110° , and melts at $159.5\text{--}160^\circ$; the *nitrate* is anhydrous. *Ethenylphenyleneamidine*, $C_6H_4 < \begin{smallmatrix} N \\ NH \end{smallmatrix} > CMe$, which is formed in association with the foregoing base, may be separated from it by its insolubility in ether, when impure; it melts at 175° , and in the pure state dissolves readily in ether.

Propylaldehydine, $C_6H_4 < \begin{smallmatrix} NPr^a \\ N \end{smallmatrix} > CEt$, from propaldehyde, is a yellow oil of bitter taste; the *hydriodide*, $C_{12}H_{16}N_2 \cdot HI + H_2O$, becomes anhydrous at 100° , and melts at $123\text{--}129^\circ$. *Propenylphenyleneamidine*, $C_6H_4 < \begin{smallmatrix} N \\ NH \end{smallmatrix} > CEt$, is separated similarly to the lower homologue; it melts at $177\text{--}178^\circ$.

Paranitrobenzylideneorthophenylenediamine,



is prepared by mixing alcoholic solutions of paranitrobenzaldehyde and orthophenylenediamine in molecular proportion. It forms red plates of metallic lustre; partial fusion takes place at 134° , becoming complete at 180° . When excess of the aldehyde is employed, *dinitrobenzylideneorthophenylenediamine*, $C_6H_4(N : CH \cdot C_6H_4 \cdot NO_2)_2$, is formed; this crystallises from chloroform in bright yellow needles which melt at 222° ; similarly to the foregoing substance, regeneration of orthophenylenediamine is effected by heating with hydrochloric acid.

Paranitrobenzenylphenyleneamidine, $C_6H_4 < \begin{smallmatrix} N \\ NH \end{smallmatrix} > C \cdot C_6H_4 \cdot NO_2$, can be prepared by boiling the alcoholic solution of nitrobenzylidene-phenylenediamine for 10 hours; it separates from nitrobenzene in hexagonal prisms which melt at 322° . The *acetate* of the anhydro-base is also formed from the mononitro- and dinitro-derivatives by warming with glacial acetic acid. It is obtained in the form of yellow needles which melt at 300° . In the latter reaction, *dinitrobenzaldehydine*, $C_6H_4 < \begin{smallmatrix} N \\ N(CH_2 \cdot C_6H_4 \cdot NO_2) \end{smallmatrix} > C \cdot C_6H_4 \cdot NO_2$, is also formed; it melts at 212.5° .

M. O. F.

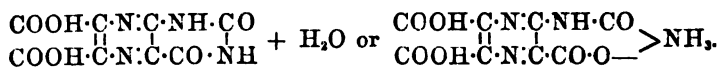
Hydrogenised Quinoxalines. By O. HINSBERG and F. KÖNIG (*Ber.*, 27, 2181—2187).—Dihydrodiphenylquinoxaline is obtained by reducing diphenylquinoxaline with stannous chloride (compare O. Fischer, *Abstr.*, 1891, 747); it forms dark yellow prisms which melt at 146°. The *stannochloride* crystallises in shining plates, bluish-black in colour. The *nitroso-derivative* forms pale yellow needles which melt at 138°.

Complete reduction of diphenylquinoxaline by means of sodium and alcohol leads to the formation of two tetrahydro-derivatives in nearly equal quantities, the isomerism which they exhibit being stereochemical in character; all attempts, however, to convert one modification into the other have hitherto been unsuccessful. α -Tetrahydrodiphenylquinoxaline, $C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CHPh} \\ | \\ \text{NH} \cdot \text{CHPh} \end{smallmatrix}$, crystallises from alcohol in colourless leaves which melt at 106°. It is readily oxidised by nitric acid and by silver nitrate, the latter producing in an alcoholic solution of the base a green coloration, which accompanies the formation of a mirror; when warmed with sulphuric acid, it develops a red tint. The *hydrochloride* melts at 225°; the *diacetyl-derivative* crystallises in needles which melt at 170°. β -Tetrahydrodiphenylquinoxaline melts at 142.5°: it is much less soluble in alcohol than the α -modification, and the reduction of silver nitrate is accompanied by a red coloration. The *hydrochloride* melts at 228°, and the *diacetyl-derivative* forms colourless prisms which melt at 192.5°.

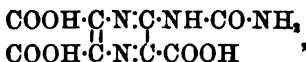
Quinoxalinedicarboxylic acid, $C_6H_4 \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{COOH} \\ | \\ \text{N} \cdot \text{C} \cdot \text{COOH} \end{smallmatrix}$ + 2H₂O, is obtained in the form of its sodium salt by the interaction of sodium dioxytartrate and orthophenylenediamine. The acid forms colourless prisms which lose water at 110°, and melt at about 190° with elimination of carbonic anhydride. On reduction with hydriodic acid, a bluish-black compound is formed, probably of the composition C₄₀H₂₈N₈O₁₆; it is acid in character, and decomposes at 170°.

M. O. F.

Oxidation of Tolualloxazine. By O. KÜHLING (*Ber.*, 27, 2116—2119).—When tolualloxazine (*Abstr.*, 1891, 1341; 1892, 70) is oxidised by means of alkaline potassium permanganate, it is converted into oxalic acid and a relatively small quantity of a new acid, which is readily separated from the former, as it forms a soluble calcium salt. To isolate the acid, the calcium salt is converted into the barium salt, and the latter decomposed by the requisite quantity of sulphuric acid. It crystallises from boiling water in slender, lustrous prisms, containing water of crystallisation, which is partly evolved on exposure to the air. It melts and decomposes at 265°, and, after drying at 110°, has the composition C₈H₆N₄O₇. It has probably one of the following constitutional formulæ.



The author regards the second of these formulæ, according to which it is a betaine-like condensation product of the acid,



as the more probable, and the examination of the metallic and alkylic salts, although not yet concluded, points to the same conclusion. The barium salt, $\text{C}_8\text{H}_8\text{N}_4\text{O}_2\text{Ba}$, forms yellowish-white, microcrystalline needles, and the silver salt a yellow, amorphous precipitate.

H. G. C.

New Reaction between Carbon Bisulphide and Primary Hydrazines. By M. BUSCH (*Ber.*, 27, 2507—2520).—When carbon bisulphide is added to an alcoholic solution of phenylhydrazine, phenylhydrazine phenylsulphocarbazine separates, and, if this is treated with alcoholic potash at a moderate temperature, it passes into solution; the filtrate deposits long, almost colourless needles of the potassium derivative of phenyldithiobiazolone hydrosulphide, $\text{C}_8\text{H}_8\text{N}_2\text{S}_2\text{K}$, which melts at about 240° . Phenyldithiobiazolone hydro-

sulphide, $\begin{array}{c} \text{NPh} \cdot \text{N} \\ | \\ \text{CS} - \text{S} \end{array} \gg \text{SH}$, is obtained on adding hydrochloric acid to a solution of the potassium salt. It crystallises in small, white needles, melts at $90-91^\circ$, boils and partly decomposes at about 230° , and becomes yellow on exposure to the air, owing to the formation of bisulphide (see below). Its acidic properties are strongly pronounced, and its salts are not decomposed by acetic acid; it is unstable towards reducing agents. The acetyl derivative, $\text{C}_8\text{H}_8\text{N}_2\text{S}_2\text{Ac}$, melts at $121-122^\circ$, and the methylic salt at $108-109^\circ$. The bisulphide, $(\text{C}_8\text{H}_8\text{N}_2\text{S}_2)_2\text{S}_2$, is best prepared by adding ferric chloride to an alcoholic solution of the hydrosulphide or its potassium salt; it crystallises in intensely yellow needles, melts at $124-125^\circ$, and, when boiled with alcoholic potash, yields the potassium salt of the hydrosulphide, together with the sulphinate $\text{C}_8\text{H}_8\text{N}_2\text{S}_2\text{SO}_2\text{K}$.

Phenyldithiobiazolonesulphonic acid, $\text{C}_8\text{H}_8\text{N}_2\text{S}_2\text{SO}_3\text{H}$, is obtained as potassium salt by treating an aqueous solution of the potassium salt of phenyldithiobiazolone hydrosulphide with potassium permanganate, and evaporating the filtrate; the salt, so obtained, forms yellow needles, and melts at 268° .

Phenyldithiobiazolone hydrosulphide, $\begin{array}{c} \text{NPh} \cdot \text{N} \\ | \\ \text{CO} - \text{S} \end{array} \gg \text{SH}$, is prepared by adding carbon bisulphide to phenylhydrazine dissolved in alcohol, and treating the resulting paste with alcoholic potash, whereby potassium phenylsulphocarbazine is obtained; this is then suspended in benzene and treated with carbon oxychloride. The hydrosulphide forms stout needles, and melts at $86-87^\circ$; the bisulphide, $(\text{C}_8\text{H}_8\text{N}_2\text{OS})_2\text{S}_2$, melts at $78-79^\circ$.

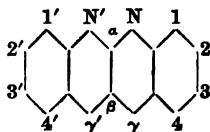
Phenylpentahydro-1:3:5-diazthine, $\text{NPh} \langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{NH} - \text{CS} \end{array} \rangle \text{S}$, is obtained by heating potassium phenylsulphocarbazine with ethylene dibromide; it forms tufts of needles, and melts at 94° . The hydrochloride,

$C_9H_{10}N_2S_2 \cdot HCl$, melts and decomposes at 188° , and the *acetyl*-derivative, $C_9H_8N_2S_2Ac$, is an oil.

Thiobiazolone hydrosulphide, $\begin{array}{c} N \cdot N \\ \diagup \quad \diagdown \\ SH \cdot C \cdot S \end{array} > C \cdot SH$, is obtained by adding a mixture of carbon bisulphide and alcohol to an aqueous solution of hydrazine sulphate, and boiling the mixture with alcoholic potash; the *hydrazine* salt, $C_4H_8N_2S_3 \cdot N_2H_4$, so obtained, melts at 185° . The *hydrosulphide* is prepared by decomposing the latter salt with hydrochloric acid; it forms stout, yellow crystals, and melts at 168° . The *potassium* salt melts at 285° with decomposition; the *monobenzoyl*-derivative melts at about 220° , the *dibenzoyl*-derivative at 184 – 185° , and the *dibenzyl*-derivative, $C_{12}N_2S_3(CH_2Ph)_2$, at 89° .

A. R. L.

Hydronephthinalines. By A. REISSERT (*Ber.*, 27, 2244–2260; compare this vol., i, 385).—The name naphthinaline is given to a base of the following formula, the various substitution products being distinguished by means of the symbol shown.



Diorthonitrodibenzylacetic acid, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2 \cdot CH \cdot COOH$, is obtained by heating ethylic diorthonitrobenzylmalonate with hydrochloric acid of sp. gr. 1.19 at 190° . It crystallises from dilute alcohol in delicate, almost white needles, melting at 149° , and is very sparingly soluble in water, readily in alcohol, &c. The *ammonium* salt, $C_{16}H_{14}N_2O_6 \cdot NH_3 + \frac{1}{2}H_2O$, forms long, silky needles, and melts, after decomposing to some extent, at 120° . The *ethylic* salt crystallises in flat, white prisms, and melts at 62° .

Orthoparadinitrodibenzylacetic acid is also obtained when impure orthonitrobenzyl chloride is used. It forms microscopic, flat needles, melting at 131° .

Δ^N -*Tetrahydro- α -naphthinaline* [$H_4 = \beta : \gamma : \gamma' : N'$] is best obtained by reducing dinitrodibenzylacetic acid in alcoholic solution with hydrogen chloride and zinc dust. It forms colourless plates, with a silvery lustre, melts at 211 – 212° , and decomposes a few degrees above this temperature. It is readily soluble in alcohol, &c., very sparingly in water. The *hydrochloride* crystallises with $2H_2O$ in long, soft, light yellow needles, or, with $1H_2O$, in hard, pointed, light yellow, well-developed prisms. It is very sparingly soluble in aqueous hydrochloric acid; the anhydrous compound melts at about 270° . The *sulphate* is also yellow, and is very sparingly soluble in water, somewhat more readily in alcohol; it melts at 222° . The *picrate* forms yellow prisms, which melt and decompose at 208° . The *platinochloride* melts and decomposes violently at 271° , and the *aurochloride* at 192° . The *mercurochloride* forms lustrous, yellow needles and melts at 232 – 233° .

$\Delta^N N'$ -*Methyltetrahydro- α -naphthinaline* [$Me = N'$] is obtained when

the base is treated with an excess of methylic iodide. It forms lustrous, almost white plates, melting at 114° . $\Delta^{N,N'}$ -Acetyltetrahydro- α -naphtholine, $C_{14}H_{13}N_2Ac$, forms small needles, melting at 240° . It is soluble in warm aqueous acids.

Dibromotetrahydronaphtholine, $C_{14}H_{13}Br_2N_2$, is formed by the action of bromine water on an aqueous solution of the hydrochloride of the base. It separates from acetic acid in brownish-yellow, compact needles, containing 3 mols. of acetic acid, which are lost at 100° , yellow crystals being left, which melt at 244° .

$\Delta^{N,N'}$ -Dihydro- α -naphtholine [$H_2 = N' : \gamma$]. Oxidising agents convert the tetrahydro-compound into this substance, and it is also obtained when the tetrahydro-compound is distilled with zinc dust. It has not hitherto been found possible to prepare naphtholine itself. The dihydro-derivative is best prepared by the use of mercuric acetate. The hydrochloride forms small, deep orange-yellow crystals, and melts at about 230° ; it is less readily soluble in water and alcohol than the corresponding tetrahydro-derivative. The free base crystallises from alcohol in lustrous, almost white plates, melting at 201° . The solutions of the base and its salts show a strong, green fluorescence; the vapours from hot solutions of the base cause great irritation of the skin of the face. The picrate melts and decomposes at 241° , the platinichloride and mercurichloride do not melt below 300° , and the aurochloride forms deep red needles.

$\Delta^{N,N'}$ -Acetyldihydro- α -naphtholine, $C_{14}H_{11}N_2Ac$, forms lustrous, white crystals, melting at 174° . The dihydro-compound, therefore, is a secondary base, and its stability towards oxidising agents is probably to be accounted for by the asymmetrical distribution of the hydrogen atoms.

Hexahydro- α -naphtholine [$H_4 = \alpha : \beta : N : N' : \gamma : \gamma'$] is obtained by the addition of sodium to a boiling alcoholic solution of the tetrahydro-base. It forms long, white needles, containing $\frac{1}{2}H_2O$, which melt at 128° . Both the free base and its salts readily oxidise in the air. The picrate is readily soluble in alcohol. A. H.

Conium Alkaloids. By R. WOLFFENSTEIN (*Ber.*, 27, 2611—2615).—The angle of rotation observed for a specimen of pure coniine being abnormally high ($+16.4^{\circ}$ in a 0.992 decimetre tube at 19°), the base was purified by conversion into the hydrogen tartrate. On treating with potash the filtrate from the crystals of this salt, it yielded a mixture of bases, from which *d*-coniine was removed in the form of the nitroso-derivative; the residual base was *n*-methylconiine (compare Passon, *Abstr.*, 1891, 1118). The observed angle of rotation for *n*-methylconiine in a 0.333 decimetre tube is $+22.6^{\circ}$.

The author draws attention to some slight confusion which has crept into the literature of this subject. M. O. F.

Coniine. By R. WOLFFENSTEIN (*Ber.*, 27, 2615—2621).—An exact description of various well-known *d*-coniine salts is given in this paper. The crystallographic examination of *d*-coniine platinichloride reveals the fact that a small quantity of the base was present in Ladenburg's isoconiine (*Abstr.*, 1893, i, 442), the latter, therefore,

has a specific rotatory power lower than that ascribed to it (*loc. cit.*).

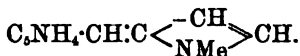
The picrate of *d*-coniine crystallises in small, yellow prisms, and melts at 75°. The aurochloride melts at 77°; the golden-yellow crystals of this salt belong to the rhombic system, the axial ratio being 0.3822 : 1 : 1.2221. The hydrochloride melts at 217.5–218.5°, the hydrobromide at 211°, and the hydriodide at 165°, the cadmio-iodide melting at 118°. The acid tartrate melts at 54°.

M. O. F.

Constitution of Nicotine. By F. BLAU (*Ber.*, 27, 2535–2539; compare *Abstr.*, 1893, i, 489).—The author's previous work on this subject has proved that nicotine consists of a pyridine nucleus combined with a closed chain containing a nitrogen atom linked to a methyl group; whilst Pinner regards it as a methylpyrrolidine trimethyleneimine ring, he believes it to be an ethyleneimine ring, and, at present, it is impossible to decide definitely between these views.

Isodipyridine, prepared by Cahours and Etard by the oxidation of nicotine, is termed by the author *nicotyrine*, and is more readily obtained by acting on nicotine with moist silver oxide; its purification is somewhat difficult. It boils at 149° (150° corr.; 15 mm.), and at 273–274° (280° corr.; 744 mm.). The yield is about 16 per cent. of the nicotine employed, of which about 38 per cent. is recovered. The iron reaction, mentioned by Cahours and Etard, is not characteristic for this base; it gives a dark coloration with isatin and sulphuric acid; a pine-wood splinter moistened with the base and then treated with hydrochloric acid is coloured dirty bluish-green, but the reaction is not very delicate. The base combines with 1HCl; the *picrate*, $C_{16}H_{16}N_2 \cdot C_6H_3N_3O_7$, is crystalline, and melts at 163–164°. The platinochloride decomposes at 120°; it is doubtful whether it contains $1\frac{1}{2}H_2O$ or $2H_2O$. The *methiodide*, $C_{10}H_{16}N_2MeI$, crystallises in lustrous, pale yellow needles, melting at 211–213°. The *ethiodide* resembles the preceding compound, and melts at 173.5–174.5°. In spite of many attempts under varied conditions, these were the only additive compounds of nicotyrine and methyl iodide or ethyl iodide which could be obtained; nicotyrine appears, therefore, to be a pyrroline

derivative, $C_8NH_4C \begin{array}{c} \diagup CH \\ \diagdown CH \\ \diagup NMe \end{array} \diagdown CH$; this accords with its production from nicotine better than such a formula as



Attempts to eliminate the quaternary pyridine nucleus from nicotyrine by oxidation, and by fusion with potash, were unsuccessful.

In continuation of his investigations on the estimation of alkyl groups linked to nitrogen (this vol., ii, 219), Herzig finds that both hexahydronicotine and octohydronicotine contain a NMe-group.

J. B. T.

Cinchotone or Hydrocinchonine. By W. KOENIGS and J. HOERLIN (*Ber.*, 27, 2290—2292).—*Cinchotone chloride*, $C_{19}H_{21}N_3Cl$, is obtained by treating cinchotone hydrochloride with phosphorus pentachloride in chloroform solution. It crystallises well from ether and melts at 85—87°.

Dihydrocinchine, $C_{19}H_{21}N_3$, is obtained by boiling the preceding compound with alcoholic potash in a reflux apparatus. It crystallises in beautiful, white leaflets, melts at 145°, and, when heated with aqueous phosphoric acid at 170—180°, yields cincholeupone and lepidine. The *picrate* melts at 195°. It is therefore identical with the dihydrocinchene obtained from commercial cinchonine.

Cinchotone, when oxidised with chromic acid solution, yields cincholeupone which melts and decomposes at 236°, and yields a hydrochloride melting at 198—200°, and an aurochloride melting and decomposing at 203°. The authors were unable to detect cincholeuponic acid amongst the products of oxidation.

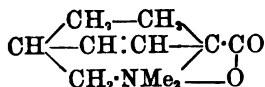
E. C. R.

Isobutylcinchonine Hydrobromide. By F. VIAL (*J. Pharm.*, [5], 30, 52—55).—Cinchonine (10 parts), isobutylic bromide (5 parts), and isobutylic alcohol (10 parts) are heated in a sealed tube at 100°. The product of the action is distilled in a current of steam, the residue extracted with water, and the concentrated solution set aside to crystallise. The solution of the crude crystals may be freed from the accompanying red colouring matter by extraction with chloroform.

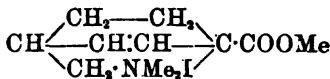
Isobutylcinchonine hydrobromide, $C_{19}H_{21}N_3O \cdot C_4H_9 \cdot HBr + H_2O$, forms colourless orthorhombic crystals, the full measurements of which are given; when dehydrated, it melts at 176°; it dissolves in water and in alcohol, but not in ether or chloroform. Its rotatory power in aqueous solution is $\alpha_D = +125^\circ$ ($p = 1$ in 100 v ; $t = 17^\circ$).

A. G. B.

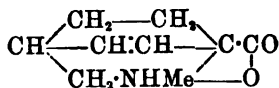
The Methylbetaine of Anhydroecgonine. By A. EINHORN and R. WILLSTÄTTER (*Ber.*, 27, 2439—2454).—The substance supposed (*Abstr.*, 1893, i, 378) to be paradimethyldihydrobenzylaminecarboxylic acid cannot have this constitution, for its methiodide, when boiled with aqueous soda, yields not trimethylamine, but dimethylamine. It is probably the methylbetaine of anhydroecgonine, with the formula given below; when it unites with hydrogen iodide or methylic or ethylic iodide, the anhydride ring is broken, and the methiodide of anhydroecgoninic acid, or of its methylic or ethylic salt, is formed. This change in its formula necessitates similar changes in the formulæ of other allied compounds; these new formulæ are given below, the old name, when it differs from the new one, being enclosed in brackets. Cocaine hydriodide, it may be said, probably stands in the same relation to benzoylecgonine as the methiodide of methylic anhydroecgoninate does to anhydroecgonine methylbetaine.



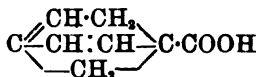
Anhydroecgonine methylbettaïne.
(Paradimethyldihydrobenzylaminecarb-
oxylic acid.)



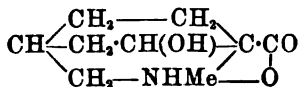
Methiodide of methylic anhydroecgo-
ninate.



Anhydroecgonine.



Paramethylenedihydrobenzoic
acid.



Ecgonine.

The compound formed by the addition of methylic iodide to anhydroecgoninemethylbettaïne is identical with the methiodide of methylic anhydroecgoninate; when boiled with aqueous soda, it yields dimethylamine. When the methylbettaïne is heated with ethylic iodide, the main product is identical with the methiodide of ethylic anhydroecgoninate, but, doubtless owing to the action of some hydriodic acid formed by a secondary reaction, some of the methiodide of anhydroecgoninic acid itself is produced; this is the sole product when the methylbettaïne is heated with ethylic iodide in absolute alcoholic solution. When the methylbettaïne is heated with absolute alcohol and sulphuric acid, and the product saturated with potassium carbonate, being carefully cooled during the operation, there are formed an oily base soluble in ether, not yet fully investigated, and a neutral substance, insoluble in ether. The latter still contains a NMe_2 - and a COOEt -group, together with the anhydroecgonine ring, for potassium carbonate decomposes it into dimethylamine and ethylic paramethylenedihydrobenzoate; hydrochloric acid converts it, at the ordinary temperature, into the methochloride of ethylic anhydroecgoninate, and at the temperature of the water bath, into alcohol and the methochloride of anhydroecgoninic acid; hydriodic acid forms the methiodide of ethylic anhydroecgoninate. If, in the above reaction, the saturation with potassium carbonate is carried out without cooling being resorted to, the nitrogenous substance is at once decomposed into dimethylamine and ethylic paramethylenedihydrobenzoate; this boils at $225-227^\circ$, and is attacked by potassium permanganate in the cold, differing in this respect from its isomeride, ethylic paratoluat, which boils at the same temperature.

C. F. B.

Ergot of Rye. By KELLER (*J. Pharm.*, [5], 30, 67-70).—The author is of the opinion that there is but one alkaloid in ergot of rye, for the properties of the sole alkaloid which he could obtain proved to be identical with those of Tanret's ergotinine, Blumberg's picrosclerotine, and Kobert's cornutine. He therefore proposes that

cornutine be retained as the name for this alkaloid, and that the other words be expunged from chemical literature. A. G. B.

Hydrolysis of Nucleic acids. By A. KOSSEL and A. NEUMANN (*Ber.*, 27, 2215—2222; compare this vol., i, 156).—When adenylic acid, prepared from the thyroid gland of the calf, is heated at 150° with 20 per cent. sulphuric acid, it is converted into thymine, a new base cytosine, ammonia, levulinic acid, formic acid, and phosphoric acid. Thymine, when quite pure, has the molecular formula $C_5H_8N_2O_2$, and not the more complicated formula $C_{23}H_{28}N_8O_6$, which was previously assigned to it.

Cytosine, $C_7H_{10}N_4O_4 + 5H_2O$, is precipitated by phosphotungstic acid, and crystallises from a faintly ammoniacal solution in rectangular tablets. It is readily soluble in hot water, very sparingly in alcohol, and insoluble in ether. The water of crystallisation is completely lost at 100°. The *sulphate* of the base crystallises in needles, the *hydrochloride* in prisms, whilst the *nitrate*, *platinochloride*, and *aurochloride* are also crystalline. Potassium bismuthiodide produces a brick-red precipitate with dilute solutions of this base, whilst silver nitrate gives a precipitate which dissolves in hot dilute ammonia, and crystallises out on cooling. The *picrate*, $C_{21}H_{20}N_{10}O_4 \cdot 2C_6H_3N_3O_7$, forms yellow needles. The yield of cytosine amounts to about 2 per cent. of the nucleic acid employed.

The presence of levulinic acid among the products of decomposition is significant, and shows that adenylic acid contains a carbohydrate group. This is in agreement with the result obtained by Kossel in the case of the nucleic acid prepared from yeast. A. H.

Vegetable Proteids. By W. PALLADIN (*Zeit. Biol.*, 31, 191—202).—An examination of the various vegetable proteids described by Weyl, Vines, Martin, Green, Chittenden, Osborne and others, leads the author to the following general conclusions:—

1. Plant-vitellin has many of the properties of albumoses.
2. Plant-myosin is only a calcium compound of vitellin.
3. The existence of vegetable albumoses soluble in water is questionable.
4. Vegetable proteids are accompanied by a still unknown nitrogenous substance.
5. The number of hitherto described vegetable proteids is greater than the number which really exist in the plants.

W. D. H.

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